PROCESS DESIGN, SIMULATION AND INTEGRATION OF DIMETHYL ETHER (DME) PRODUCTION FROM SHALE GAS BY DIRECT AND INDIRECT METHODS

A Thesis

by

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Submitted to the Office of Graduate and Professional Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

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August 2014

Major Subject: Chemical Engineering

ABSTRACT

As the energy demand is increasing constantly, sustainable energy resources are needed to meet this demand and enable economic stability. In order to attain this goal, researchers continue to develop new technologies and methods in the field of sustainable energy. Over the last decade, the U.S has witnessed substantial growth in shale gas production. Consequently, shale gas has become a competitive feedstock for usage as energy and production of chemicals and petrochemicals.

A valuable product which may be obtained from shale gas is dimethyl ether (DME). Dimethyl ether can be used in many areas such as power generation, transportation fuel, and domestic heating and cooking. Dimethyl ether is currently produced from natural gas, coal and biomass through synthesis gas as an intermediate. Recently, the attention to DME has increased because of its potential in addressing energy security and environmental problems.

DME is produced conventionally through two steps (indirect process) which are methanol synthesis and dehydration of the methanol to DME. Another way to produce DME is the direct synthesis of DME from syngas. In order to use DME as a fuel alternative, it must be produced at low cost in large quantities. The purpose of this study is to develop a process synthesis, simulation, and integration of a shale gas-to-DME plant by direct and indirect methods. Techno-economic analysis is carried out to assess the profitability of the base-case processes under current market conditions. A sensitivity analysis is also conducted to evaluate the process profitability under variable market

conditions. Finally, the both methods are compared in terms of the fixed capital cost, operating cost, return on investment, and CO_2 and water impact.

Indirect and direct process simulation of commercial DME plant was carried out by Aspen Plus. The shale gas feedstock was taken from one of the wells in Barnett shale play. The DME production capacities of the base cases for the direct and indirect processes were set to 3,250 tonnes per day. The direct and indirect process flowsheets were synthesized using five and seven main processing steps, respectively. Pinch analysis was used to conduct heat integration of the process. As a result of study, it was found that the direct method has advantage over the indirect method in terms of the fixed capital cost, operating cost, return on investment, and CO2 impact.

The capital investment of the direct production method is 25% less than the indirect method. The direct method is more economically attractive than the indirect method. When a sensitivity analysis is considered, the prices of methanol and shale gas are the most important factors impacting the operating cost. The contribution of energy integration on the ROI of the direct method is approximately 2.25%. The ROI of the indirect method is improved by 1.83% after energy integration. In contrast to the other criteria, the indirect way has significant advantage over the direct way by producing almost 1760 ton/d water. The direct method produces less CO_2 emission than the indirect method because it uses dry reforming to convert CO_2 to syngas.

DEDICATION

To

My parents

My brother

And

My friends

ACKNOWLEDGEMENTS

All the praises are due to Allah, the Most Beneficent and the Most Merciful for blessing me with the ability to pursue my graduate studies and seek knowledge.

I would like to thank my advisor, Dr. Mahmoud El-Halwagi for providing me the opportunity to work with him and for his constant support and guidance throughout my study. I would like to also thank my committee members, Dr.M.Sam Mannan and Dr. Hisham Nasr-El-Din.

Thanks are extended to my colleagues for their support and help. Special thanks to Ali Alshehri and Kerron Gabriel.

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NOMENCLATURE

ABBREVIATIONS

C2 – ethane

C3 – propane

kW– kilowatt

MeOH – methanol

MMscf – million standard cubic feet

MMBtu – million Btu (British thermal unit)

ROI – return on investment

WGS –Water gas shift

DME- Dimethyl ether

GTL- Gas-to-liquids

WTT- Well-to-tank

FCI- Fixed capital investment

WCI- Working capital investment

TCI- Total capital investment

1 INTRODUCTION

1.1 Natural Gas

Global energy demand is increasing constantly. According to the International Energy Agency, the increase is expected to be approximately 41% between 2009 and 2035 (**Fig. 1-1**). Therefore, sustainable energy resources are needed to meet this demand and enable economic stability. In order to attain this goal, the researches continue to develop new technologies and methods in many areas [1, 2]. Despite the use of alternative energy sources, 82% of the United States' energy needs are still produced from fossil fuels [3].

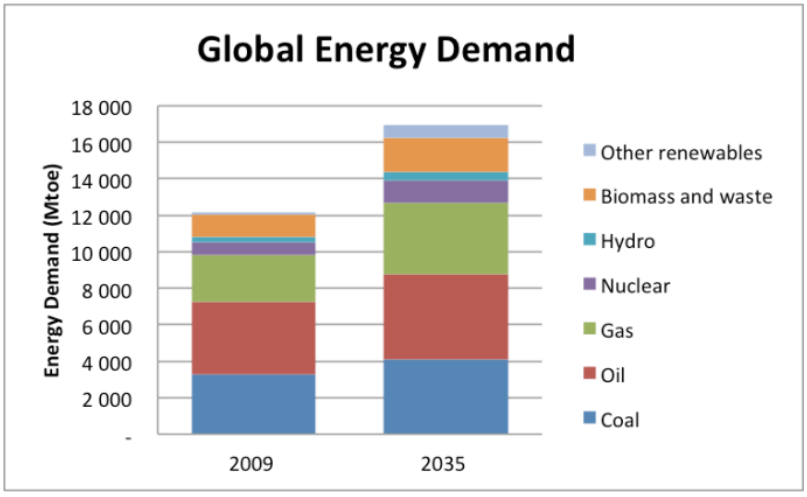

Fig. 1-1 The increase of global energy demand between 2009 and 2035. (Data were extracted from the international energy agency 2011).

Natural gas is one of the biggest contributors among fossil fuels. Based on the 2010 International Energy Agency report, its contribution is approximately 22 % of total energy production (**Fig. 1-2)**. Natural gas is composed of methane butane, ethane, propane, and other gases. However, methane is the main component of natural gas and its percentage changes between 80-95% in typical composition (**Table 1-1**). Natural gas is odorless, colorless, and it is more environmentally friendly than coal and oil due to its clean burning [4, 5].

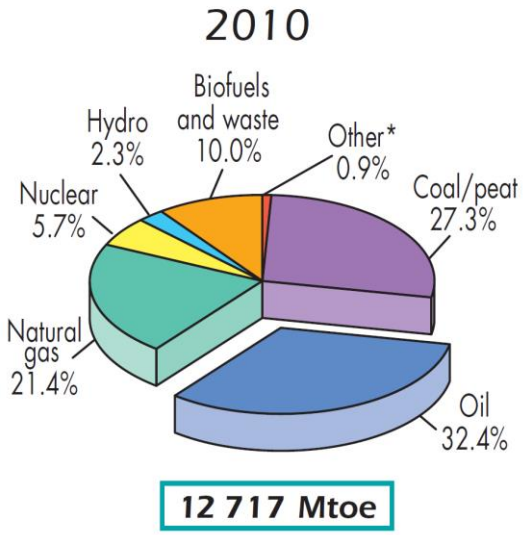

Fig. 1-2 The contributions of different sources in U.S energy supply. (Data were extracted from the international energy agency 2011).

Natural gas is found in rock formations, and it is classified as conventional and unconventional. Until the last decade, natural gas had been produced mainly from

conventional sources, but the production of natural gas from unconventional resources has increased rapidly during last decades. Natural gas has many application sectors such as industrial, residential and commercial due to its versatility. Its biggest advantage over the other fossil fuels is having characteristic of efficiency and clean burning. This makes it environmentally friendly compared to the other fossil fuels. Natural gas retains its importance in the energy world's future plans. Especially, natural gas has a big effect on U.S economy because of its feature of reliability. Thus, 84% of natural gas is produced in the United States [6, 7].

Table 1-1 Chemical Composition of Conventional Natural Gas [8].

Components	Chemical formula	Typical Com. (mol %)	Extreme (mol%)
Methane	CH_4	80 – 95	50 – 95
Ethane	C_2H_6	2 – 5	2 – 20
Propane	C_3H_8	1- 3	1 – 12
Butane	C_4H_{10}	0 – 1	0 – 4
C5 alkanes and higher hydrocarbon	C_5+	0 – 1	0 – 1
Carbon Dioxide	CO_2	1 – 5	0 – 99
Nitrogen	N_2	1 – 5	0 – 70
Hydrogen Sulfide	H_2S	0 – 2	0 – 6
Oxygen	O_2	0	0 – 0.2
Helium	He	0 – 0.1	0 – 1
Other inert gases	traces		

1.2 What is Shale Gas?

Natural gas is classified as conventional and unconventional. One characteristic of conventional natural gas is that found in rocks, which have a permeability of more

than 1000 microdarcy. On the other hand, the unconventional natural gas is situated in rocks with a permeability of less than 1 milidarcy. Shale gas, tight gas, gas hydrates and coal-based methane are main types of unconventional natural gas [6]. Shale gas is found in shale deposits, and it is the source and the reservoir for natural gas. Shale gas has the cleanest burning compared to other fossil fuels, and it has the biggest portion in future energy plan to supply energy need and decreasing greenhouse gas emissions [9].

The production of natural gas from shale formations is needed more advanced technologies than the conventional way. However, contribution of unconventional resources to natural gas has increased rapidly during last decade. For example, approximately 65% of natural gas is produced from unconventional resources in North America. Shale gas has the biggest effect on this growth among unconventional resources [10].

1.3 Shale Gas Revolution in U.S

The low permeability of shale gas does not allow high quantity production. However, the combination of horizontal drilling and hydraulic fracturing, and the technological advancements in these both areas enable to extract huge quantities of natural gas from shale formations. This is the key point that allows shale gas to be economically feasible [7, 11]. **Fig. 1-3** shows unconventional deposits over the world.

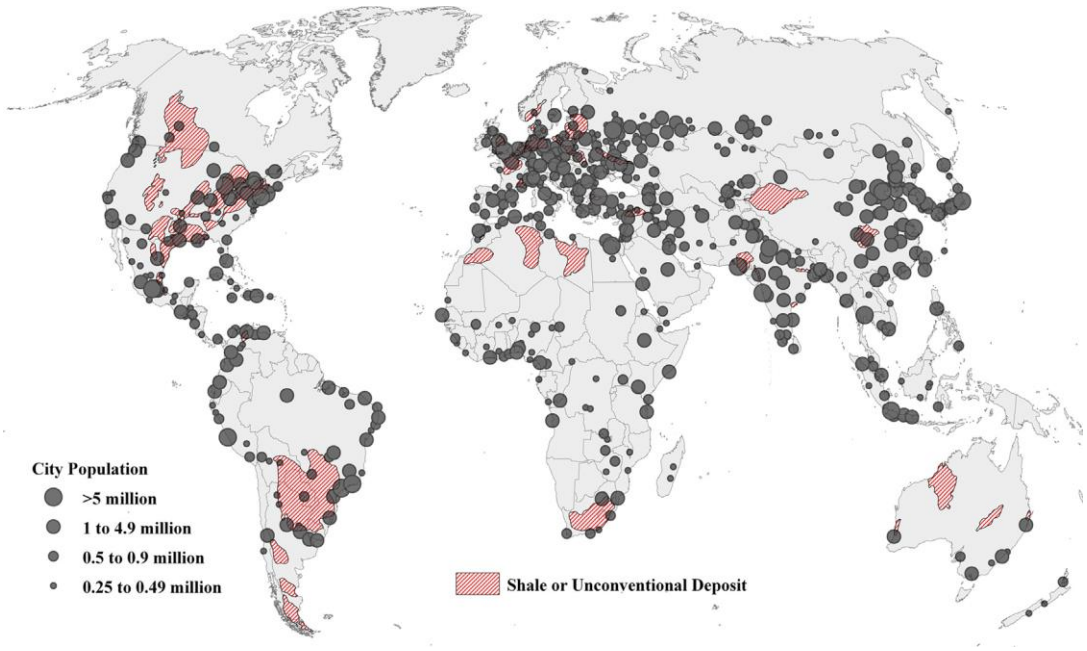

Fig. 1-3 Unconventional deposits over the world [10].

Over the last decade, the U.S has shown huge development in shale gas production. The first economical shale gas production was carried out in Barnet (United States) and there are more than 40,000 wells around 20 states currently. As result of this revolution, shale gas production increased from 1% to 20% in 10 years (from 2000 to 2010). According to The Energy Information Administration, this amount will increase 46% by 2035 (**Fig. 1-4**). The biggest effect of this revolution is on domestic gas price that has been less than $5.00 per million British thermal units (MMBTU) [9, 11, 12].

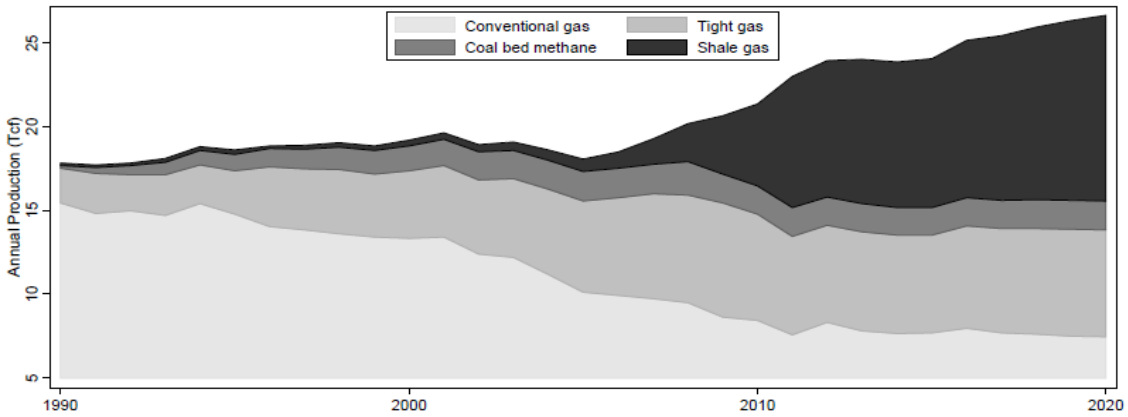

Fig. 1-4 Projection of natural gas production based on the different sources. (Data were extracted from Energy Information Administration 2013).

1.4 Shale Gas in Texas

Today, Texas is the biggest shale gas producer in the U.S. and has 7 of 35 the U.S. shale plays (**Fig. 1-5**). The Barnett, Haynesville and the Eagle Ford are the largest natural gas-producing plays in Texas. On the other hand, the Barnett is the largest of three, based on the area, wells and total production [10]. Average shale gas compositions from different wells are shown in **Table 1-2**.

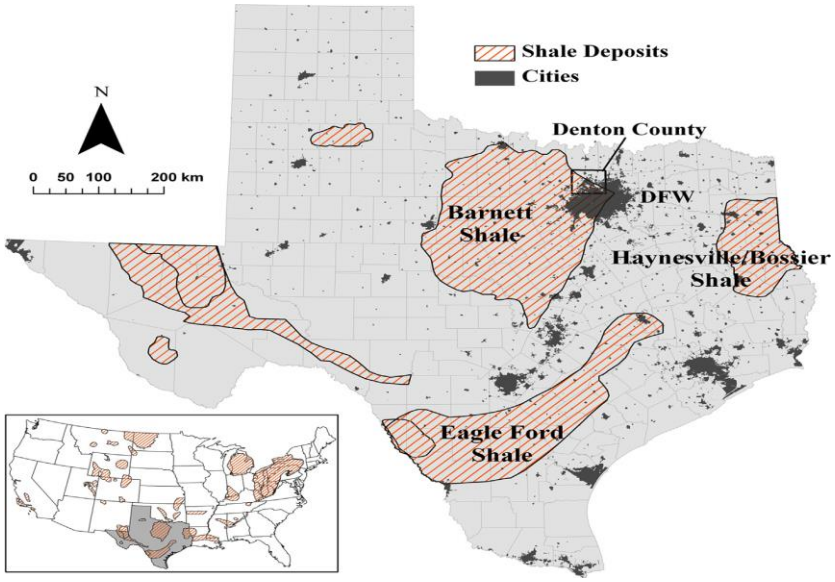

Fig. 1-5 Map of shale deposits and urban areas in Texas [10].

Table 1-2 Average Shale Gas Compositions from Wells [1].

Reservoir	Methane	Ethane	Propane	CO_2	N_2
Barnett	86.8	6.7	2.0	1.7	2.9
Marcellus	85.2	11.3	2.9	0.4	0.3
Fayetteville	97.3	1.0	0.0	1.0	0.7
New Albany	89.9	1.1	1.1	7.9	0.0
Antrim	62.0	4.2	1.1	3.8	29
Haynesville	95.0	0.1	0.0	4.8	0.1

1.5 Barnett Shale, Texas

The Barnett Shale is located in central Texas around the Dallas-Ft. Worth area. The Barnett has 16,000 producing wells and this number is the greatest among the other

shale gas-producing areas. **Fig. 1-6** represents increase of natural gas production between 2000 and 2010 in important shale plays. The number of wells in Barnett showed 16% of increment from 2009 to 2011. The Barnett is the largest gas producer in Texas and the contribution of Barnett to gas producing in Texas is almost 31% [13]. The composition of several reservoirs in Barnett can be found in **Table 1-3**.

Table 1-3 Barnett Shale Gas Composition [1].

Reservoir	Methane	Ethane	Propane	CO_2	N_2
1	80.3	8.1	2.3	1.4	7.9
2	81.2	11.8	5.2	0.3	1.5
3	91.8	4.4	0.4	2.3	1.1
4	93.7	2.6	0.0	2.7	1.0
average	86.8	6.7	2.0	1.7	2.9

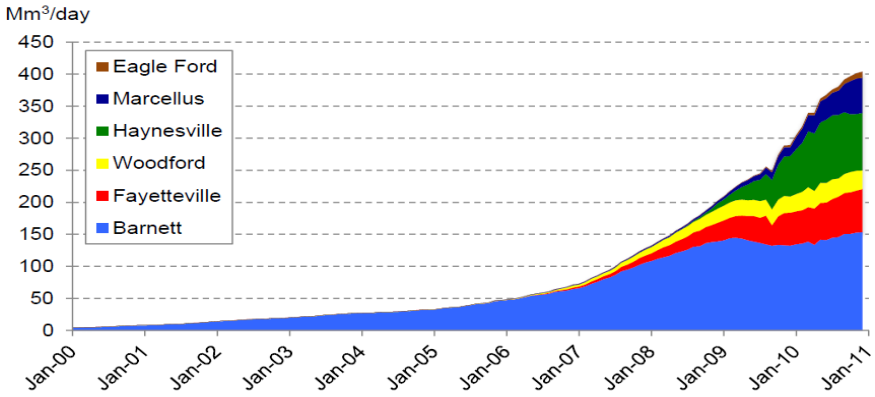

Fig. 1-6 Growth in natural gas production from U.S. shale plays between 2000 and 2010. (Data were extracted from HPDI 2012).

2 DIMETHYL ETHER (DME)

2.1 DME Properties

Dimethyl ether is the simplest Ether, non-toxic and non-carcinogenic. It has no C-C bonds and it has high H/C –ratio. DME has similar physical characteristic with LPG and this enables to store and deliver DME by using existing infrastructures with minor modifications. Thus, DME is considered to be substitute with LPG for cooking and heating purposes, but also as an aerosol propellant in spray cans. Also, DME is considered as an alternative to diesel fuel due to its high cetane number and it generates lower NOx emissions than the combustion of diesel. For these reasons, DME has high industrial interest. It can be produced from different kinds of sources such as natural gas, crude oil, residual oil, coal, waste products and bio-mass [14-16].

Table 2-1 Physical properties of DME and other fuels [17].

Properties	**DME**	**Methanol**	**Propane**	**Methane**	**Diesel fuel**
Chemical formula	CH_3OCH_3	CH_3OH	C_3H_8	CH_4	-
Boiling point (K)	247.9	337.6	231	111.5	180-370
Liquid density (g/cm^3 at 293 K)	0.67	0.79	0.49	-	0.84
Specific gravity (vs. air)	1.59	-	1.52	0.55	-
Heat of vaporization (kJ/kg)	467	1,097	426	510	-
Vapor pressure (atm at 293 K)	6.1	-	9.3	-	-
Ignition temperature (K)	623	743	777	905	-
Explosion limit	3.4-17	5.5-36	2.1-9.4	5-15	0.6-6.5
Cetane number	55-60	5	5	0	40-55
Net calorific value (10 ^{6}J/Nm^3)	59.44	-	91.25	36	-
Net calorific value (10 ^{6}J/kg)	28.90	21.10	46.46	50.23	41.86

It can be seen physical properties of DME in **Table 2-1**. The vapor pressure of DME is 6.1 atm at 293 K, so it can easily liquefied by small amount of pressure. When compare DME to propane, the DME and propane show similar physical properties. This feature of DME enables it to be used in LPG as a blend. The calorific value of DME is higher than Methanol and Methane. Ratios are 1.37 and 1.65, relatively. DME burns like a natural gas. Decomposition of DME into the troposphere does not cause greenhouse effect and ozone layer depletion [17].

2.2 DME Market

Although DME has the promising future, its production and using amount is relatively low in the world. On the other hand, the production capacity of DME had shown significant improvement between 1993 and 2012 (**Fig. 2-1**). The capacity increased from 20,000 metric tons to 11,317,000 metric tons in 20 years. The worldwide production of DME is approximately 5 million tons per annum and it is estimated that the capacity is more than 11.3 million tons globally. Asia has the biggest potential of DME market. The studies and investments have been showing increment constantly in this region. The majority of current DME is being produced in China, Japan, Korea and Brazil. Also, there are new candidates to raise capacity and production such as Egypt, India, Indonesia, Iran and Uzbekistan. In China, the annual capacity and production has increased 96% and 97% between 2002 and 2006, respectively. Moreover, China has the plan of 20 million tons of DME production capacity by 2020 [18, 19].

Approximately, 10,000 tons per year of DME is produced in Japan. The big companies (JFE, Mitsubishi, Mitsui) in Japan have a plan to reach the production of 2

million ton per year DME. South Korea is continuing the studies to commercialize DME to be energy source of the 21 century. For future progress, the expected growth of the DME market in Asia is from 18 MMTPA to 27 MMTPA by 2030 [18, 20].

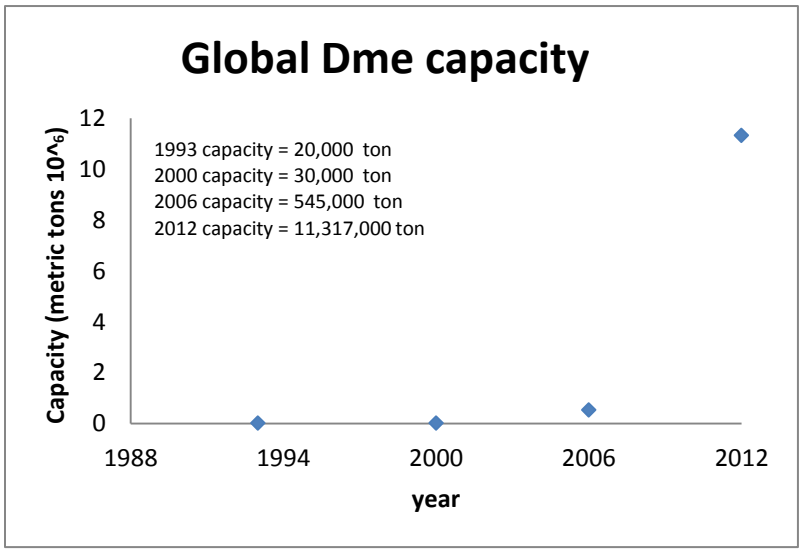

Fig. 2-1 The growth of the global DME capacity between 1993 and 2012 [21].

2.3 DME as an Alternative Fuel Candidate

The calorific value of DME for per kg is lower than methane and propane but it is higher than methanol. Because of this character of DME, more quantity of DME is needed to travel same distance in transportation compared the other conventional fuels. On the other hand, the calorific value of DME for per Nm^3 is higher than methane. In terms of safety concern, DME is safer than propane because the lower limit of explosion of DME is higher than propane [22].

DME has high cetane number and it shows characteristic of vaporizing easily during injection. Thanks to this feature, DME has low fuel injection pressure around 200 atm. However, required injection pressure of diesel is higher than 1200 atm. Well to tank (WTT) efficiency is one of the most important criteria to compare DME to other conventional fuels. Based on the **Fig. 2-2**, the WTT efficiencies of petroleum based fuels are almost 90% by having highest values. However, the WTT of DME exceeds slightly 70% [23].

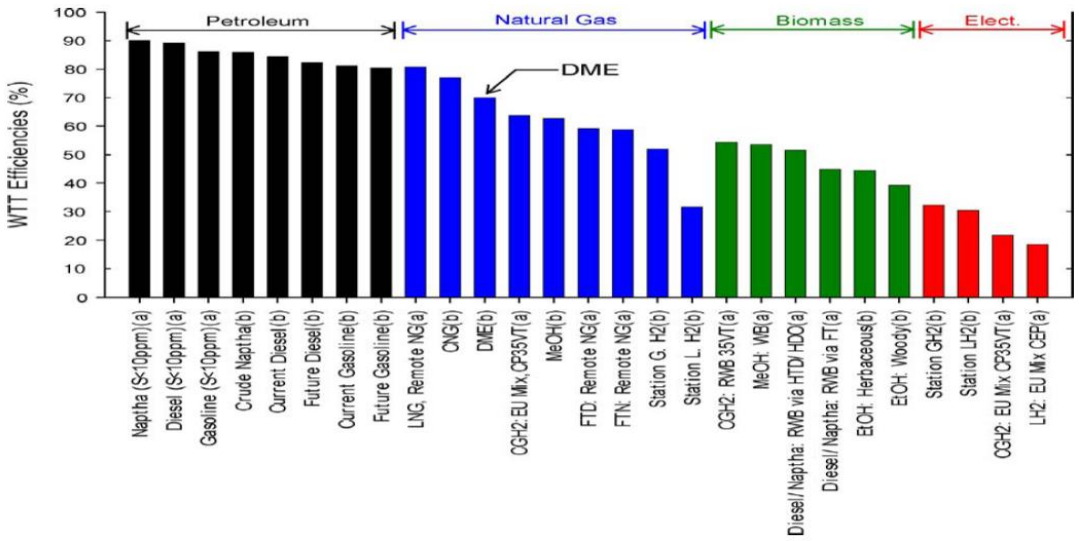

Fig. 2-2 Well to tank (WTT) efficiencies of fuels [24].

DME is an environmentally friendly fuel and this is its advantage over other fuels. The emission of NOx and CO in DME engines is lower than gas-to-liquid (GTL) and diesel engines. The CO emission of diesel and GTL is lower at low loads but the CO emission of diesel and GTL shows significant increment (**Fig. 2-3**). Conversely, the CO

emission of DME stays same level by increase of load. At the low loads, DME has the lowest emission compared to diesel and GTL. The emission of NOx increase for all fuels by high level of loads but even DME has the lowest emission (**Fig. 2-4**) [25].

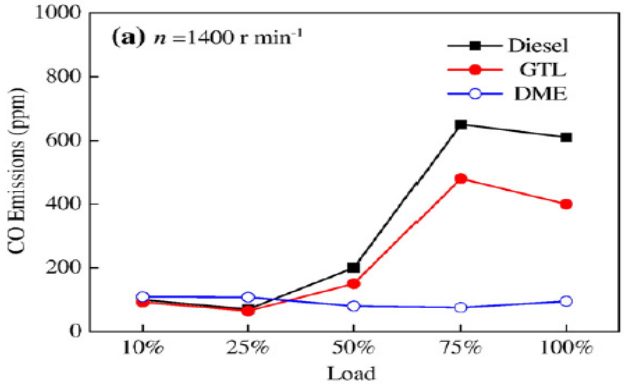

Fig. 2-3 CO emissions for engine fueled with diesel, GTL and DME at 1400 rpm [25].

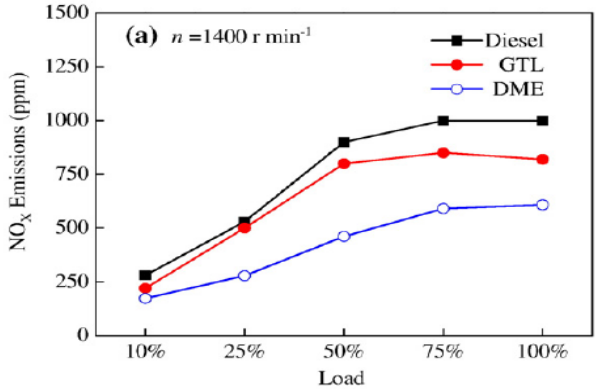

Fig. 2-4 NOx emissions for engine fueled with diesel, GTL and DME at 1400 rpm [25].

3 GAS TO LIQUIDS PROCESS (GTL)

3.1 Introduction

GTL is the process that converts the natural gas or other gaseous hydrocarbons into longer-chain hydrocarbons [26]. As seen in **Fig. 3-1** there are mainly three steps in the GTL process. The first step is to produce syngas (combination of CO and H2) from natural gas. The conversion of syngas to liquid hydrocarbons on a Fisher-Tropsch catalyst is the second step of GTL. Final step is the upgrading the reactor products by using a cracking and hydro-processing units to final products [27, 28]. Carbon based sources such as hydrocarbons, coal, petroleum coke and biomass can be used for production of syngas in GTL process. However, natural gas is the leading feedstock in industry due to its economic advantage to others [29]. Moreover, natural gas based GTL is the most developed in terms of technology and commercial compared to coal-to-liquids (CTL) and biomass-to-liquids (BTL) [30].

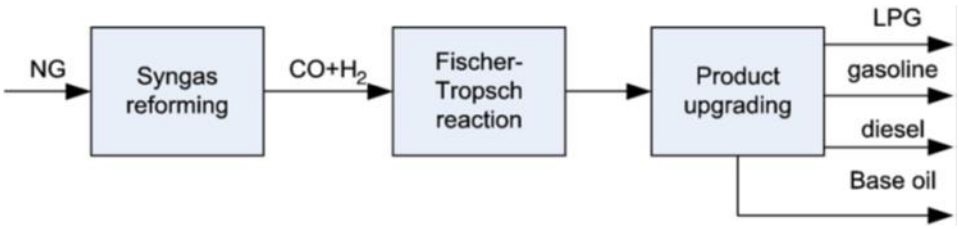

Fig. 3-1 A schematic representation of the GTL process [28].

Diesel, gasoline, liquefied petroleum gas (LPG), base oil and waxes, and petrochemicals such as naphtha and stream cracking are the basic products of GTL process [31]. The advantageous characteristic of GTL products is consisting of extremely low sulfur and aromatic compounds and showing low emission of carbon monoxide, nitrogen oxides, hydrocarbons, and other particulates. These criteria enable to be considered GTL as an environmentally friendly and GTL process has recently received much attention because of these advantages [32]. **Fig. 3-2** represents the opportunities and challenges of GTL process.

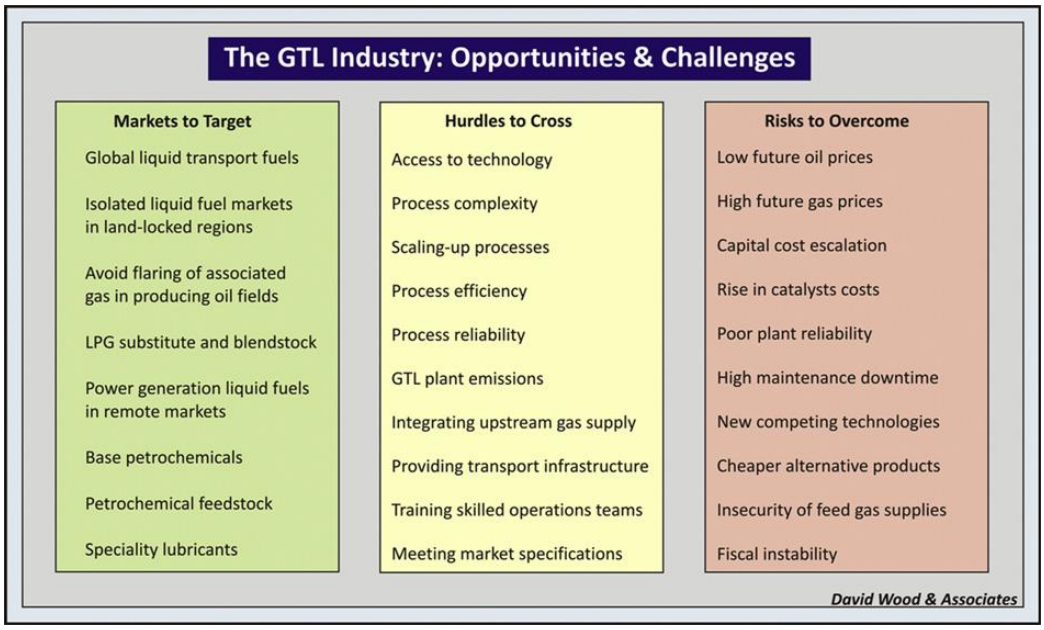

Fig. 3-2 The GTL Industry: A summary of its opportunities and challenges [33].

3.2 Syngas Reforming of GTL Process

Reforming section is the first step for GTL process and the reforming of natural gas is the main method in industry to produce syngas. There are mainly four types of reforming: partial oxidation, steam reforming, dry reforming, and combinations of these reforming. Process objectives, availability of material, energy resources, final product, energy requirement, environmental issues and safety issues are the main concepts for selection of reforming type or types [34].

3.2.1 Gasification Reactions

The main composition of syngas consists of CO and H_2. The ratio of H_2: CO is determined by reaction temperature, feedstock composition and reforming agent. Steam reforming, partial oxidation, dry reforming and autothermal reforming are the methods which used in industry for reforming processes.

3.2.1.1 Partial Oxidation of CH_4

The reaction of partial oxidation is exothermic and the residence time is very short (τ = 3.6-72 ms). The overall reaction between CH_4 and O_2 is;

$$CH_4 + 0.5O_2 \leftrightarrow CO + 2H_2 \qquad \Delta H^o\,298K = -36\ \text{kJ/mol} \qquad (3\text{-}1)$$

The partial oxidation gives a ratio of H_2: CO closely 2:1. The conversion of CH_4 increases by increase of temperature (**Fig. 3-3**) [34].

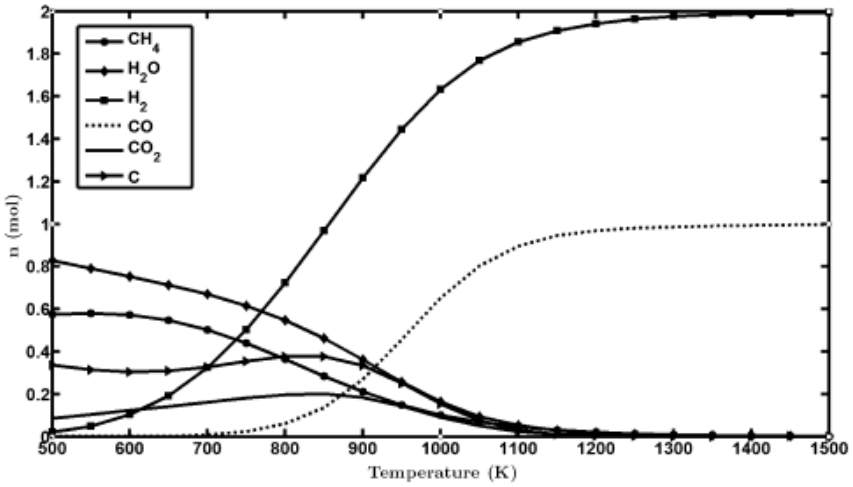

Fig. 3-3 Effect of temperature on equilibrium for POX. (CH_4:O_2 = 1:0.5) P = 1 bar [34].

3.2.1.2 Steam Reforming of CH_4

The reaction between methane and water occurs endothermic and the overall reaction is;

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H^o 298K = 206 \text{ kJ/mol} \tag{3-2}$$

Water-gas shift reaction;

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H^o 298K = -41 \text{ kJ/mol} \tag{3-3}$$

The highest H_2: CO ratio can be reached during steam reforming (3:1). Steam reforming is carried out in a multi-tubular reactor and nickel is used commonly as a catalyst. The temperature has the important role on the equilibrium composition, and higher temperature favor greater CH_4 conversation [34]. **Fig. 3-4** shows the effect of temperature on conversion of CH_4.

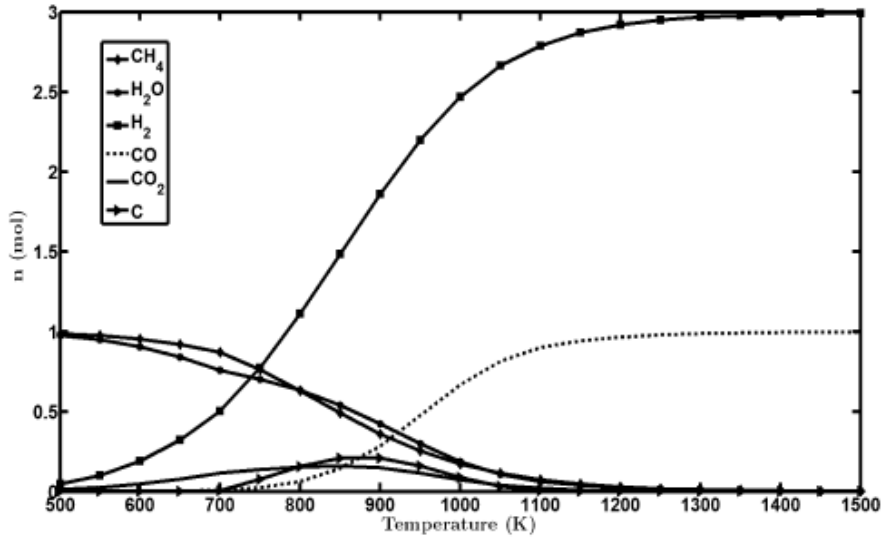

Fig. 3-4 Effect of temperature on equilibrium for SR. (CH_4:H_2O = 1:1) P = 1 bar [34].

3.2.1.3 Dry Reforming of CH_4

The reaction is endothermic, and required low pressure and high temperature. The reaction can be illustrated as follow;

$$CO_2 + CH_4 \leftrightarrow 2CO + 2H_2 \qquad \Delta Hr = 247 \text{ kJ/mol} \qquad (3\text{-}4)$$

The result of this reaction, the ratio of H_2: CO is theoretically produced around 1:1. Similar to steam reforming and partial oxidation, the higher temperatures favor the higher conversion of H_2 and CO (**Fig. 3-5**) [34].

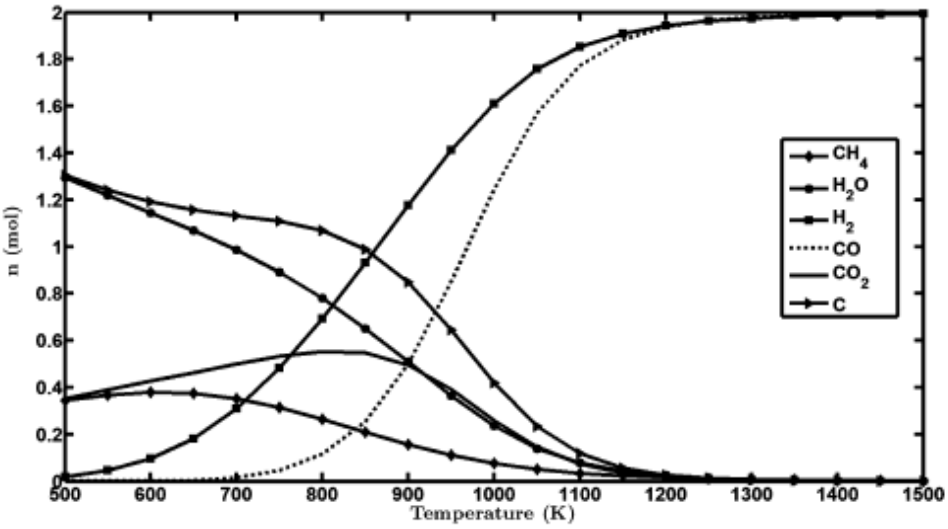

Fig. 3-5 Effect of temperature on equilibrium for dry reforming. (CH_4:CO_2 = 1:1) P = 1 bar [34].

3.2.1.4 Autothermal Reforming of CH_4

This type is the combination of combustion and steam reforming to obtain necessary H2: CO ratio. The reactions of autothermal reforming are;

$$CH_4 + 1.5O_2 \rightarrow CO + 2H_2O \quad \Delta H^o\,298K = -519\ kJ/mol \tag{3-5}$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H^o\,298K = 206\ kJ/mol \tag{3-6}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H^o\,298K = -41\ kJ/mol \tag{3-7}$$

Autothermal reforming enables better temperature control in reactor by using steam reforming and partial oxidation together. Also, it provides the opportunity to have necessary H2: CO ratio.

3.3 GTL Process Catalysts

Supported nickel, cobalt, and iron catalysts, supported noble metal catalysts and transition metal carbide catalysts are the main types of catalysts for the reforming processes. During syngas production, catalyst deactivation occurs due to carbon deposition. Thus, there are many studies of modification of the supports in order to increase the stability of the catalyst. Ni/Al_2O is the most common catalyst that is used for the reforming reaction due ti its low cost and high turnover frequency [35].

3.4 Fischer-Tropsch Synthesis

The Fischer-Tropsch Synthesis is the process that converts catalytically syngas to liquid hydrocarbons [32, 36]. The Fisher-Tropsch is a leading technology among all others in GTL process [28]. The fundamentals of the gas to liquid process were found by German scientists Franz Fischer and Hens Tropsch in 1922 [37]. Furthermore, Franz Fischer and Hens Tropsch built the first industrial Fisher-Tropsch reactor on a fixed bed reactor in 1935 [28]. Based on the technological developments, Germany was the first country to commercialize this process in 1936, and France, Japan, China and South Africa followed Germany [27].

3.4.1 Fischer-Tropsch Chemistry

There are many reactions that are occurring in FT reactors but the general form of reaction is:

$$nCO + mH_2 \rightarrow C1 - C_{40}\text{+alkanes} + H_2O \text{ or } CO_2 \quad (3\text{-}8)$$

There are also several possible reactions may occur:

$$nCO + (2n+1)\ H_2 \rightarrow C_nH_{2n+2} + nH_2O \text{ (n-paraffins)} \quad (3\text{-}9)$$

$$nCO + 2nH_2 \rightarrow C_nH_{2n} + {}_nH_2O \text{ (olefins)} \quad (3\text{-}10)$$

$$(6+n)\ CO + (2n+9)\ H_2 \rightarrow C_6{}_+{}_nH_{6+2n} + (6+n)\ H_2O \text{ (aromatics)} \quad (3\text{-}11)$$

It is possible to produce alcohols and other oxygenates but they are usually negligible. The Fischer-Tropsch reaction conditions are between 200-300 °C and 10-40 bar. Reaction catalysts are iron or cobalt based catalysts. Process conditions, catalyst and reactor type, and the ratio of H_2/CO are the key factors that determine the chain length of reactor products [27]. It is very important to provide a sufficient cooling of reactor to continue healthy reactor conditions because the reactions that occur in reactor are highly exothermic [32].

Type of reactor has significant effect on the final products in reactor. Multitubular fixed-bed reactors, circulating fluidized bed reactors, and fixed slurry bed reactors are the industrial Fisher-Tropsch's reactors (**Fig. 3-6**) [28, 36].

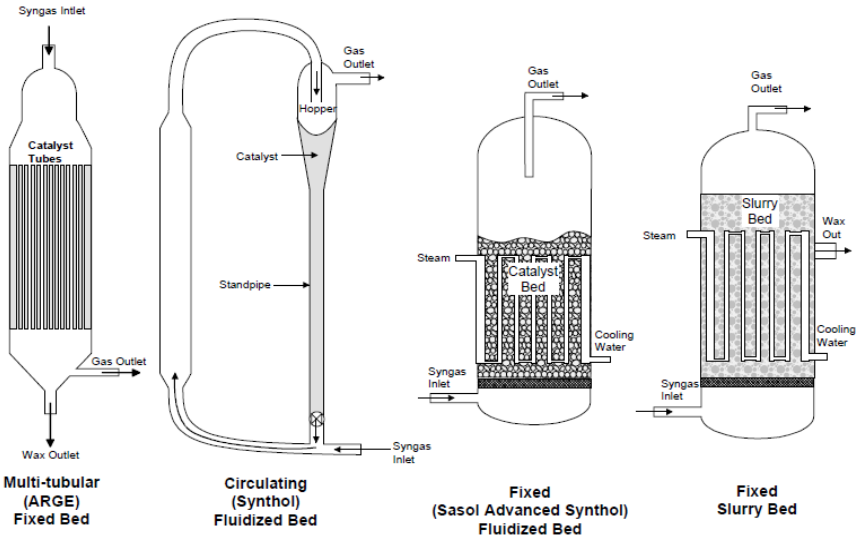

Fig. 3-6 Fischer-Tropsch reactors [38].

3.5 Product Upgrading

In product upgrading section, GTL products that obtained during FT reactions are converted to more desirable products. During FT reactions, large amount of heavy waxes are generated and later more worthy hydrocarbons are produced from these heavy waxes by using hydrocracking process [33].

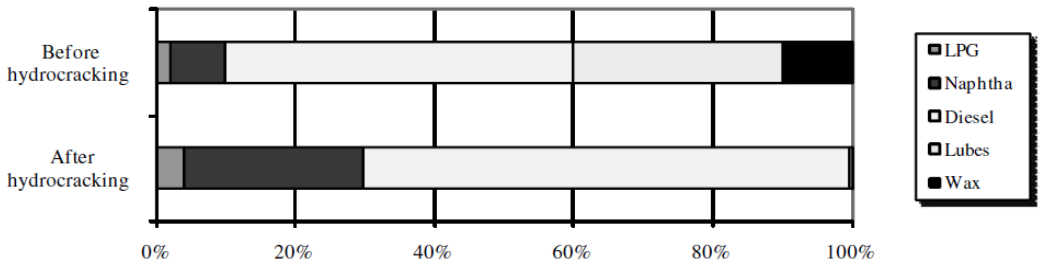

Fig. 3-7 Typical compositions of Fisher-Tropsch products before and after hydrocracking [36].

Hydrocracking is the process that heavy hydrocarbons are broken into simpler molecules by breaking C-C bonds. The hydrocracking process can be applied easier for GTL products since they are free of sulfur, nitrogen and aromatics [36]. **Fig. 3-7** represents typical compositions of Fisher-Tropsch products before and after hydrocracking.

Table 3-1 GTL products and services.

GTL products	**Services**
Naphtha	Petrochemical
Diesel	Transportation
Jet fuel	Air transportation
Wax/lube	Lubricant

3.6 GTL Market

New developments of GTL technologies and investments for new plants have increased world widely [30]**.** Exxon Mobil, Sasol, Shell, BP, Syntroleum, Rentech and Conoco are the main companies that can operate large scale GTL plants [39]. As seen from **Fig.3-8**, the total capacity of GTL plants showed huge increase between 2006 and 2011. Moreover, the increase will continue crescendo [31].

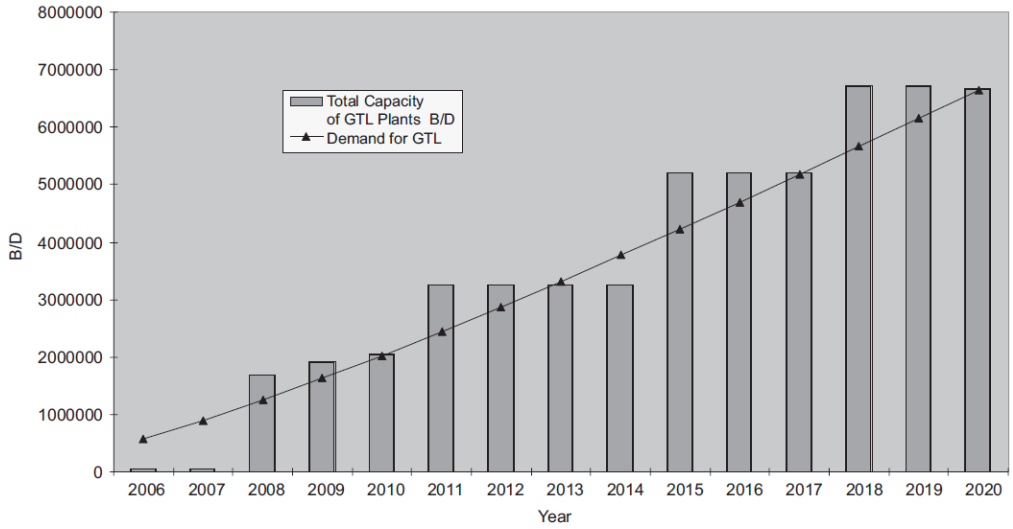

Fig. 3-8 GTL plants expansion during 2006-2020 [31].

Pearl (Qatar), Oryx (Qatar), Bintulu (Malayisia), and Mossel Bay (South Africa) are the major global GTL plants currently and the capacities of these plants are 120,000, 34,000, 14,700 and 45,000 bbl/day, respectively. It is expected that 10 new GTL plants will be constructed next ten years by having value of the range between $12 and $20 billion. The companies of Sasol, Shell, Juniper and G2X have the plan to investment of GTL plants in Louisiana (United States) [40]. Existing GTL plants over the world are shown in **Fig. 3-9** and prospective initiatives GTL plants over the world are shown in **Fig. 3-10**.

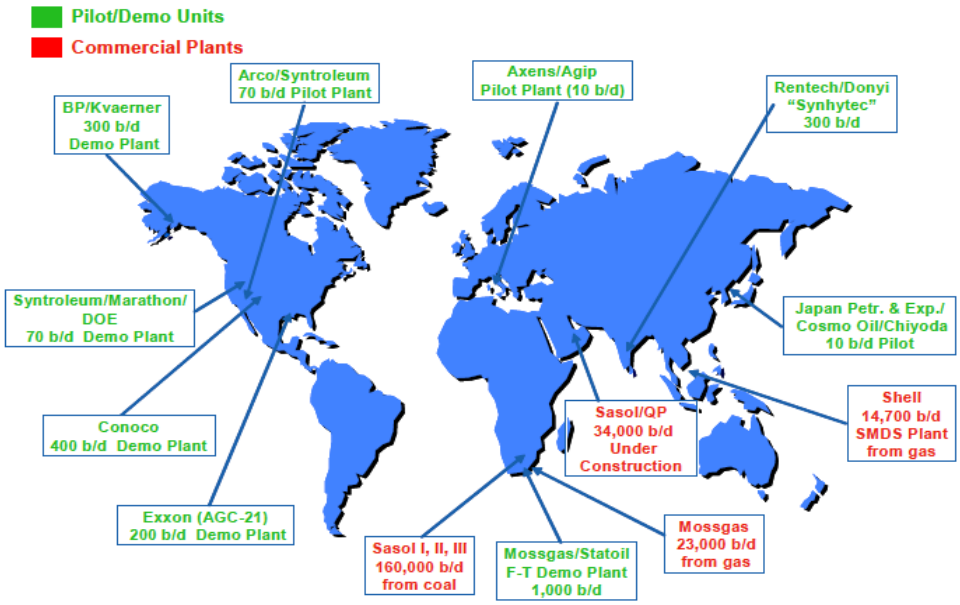

Fig. 3-9 Existing GTL plants over the world [36].

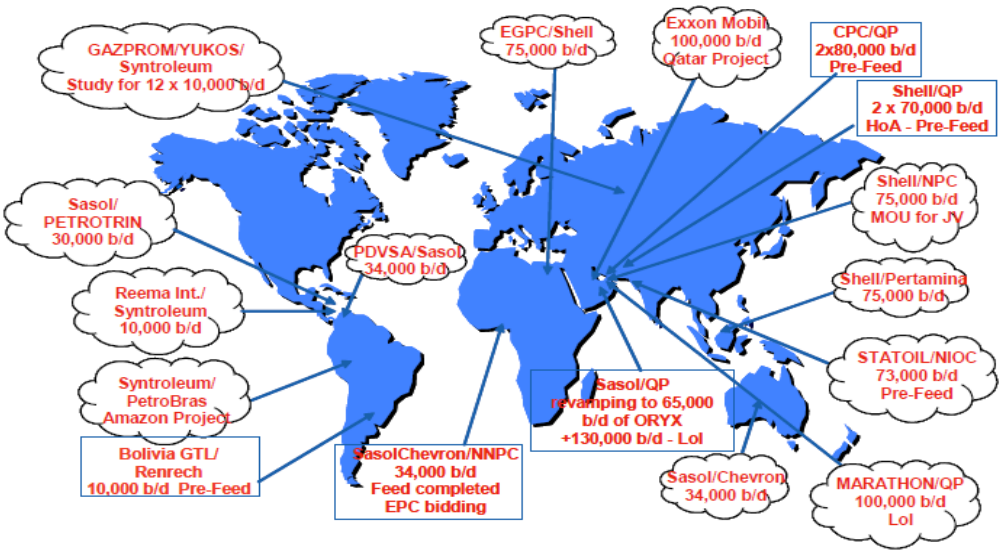

Fig. 3-10 Prospective Initiatives GTL plants over the world [36].

According to recent research, the world demand of transportation fuel will show increase. For example, it is expected that the demand of diesel will increase from 25 million barrels/day to 37 million barrels/day between 2011 and 2035 (**Fig. 3-11**). Transportation fuel is the primary sector for GTL. For this reason, the GTL technology has promising future to meet this increase in demand [33, 37].

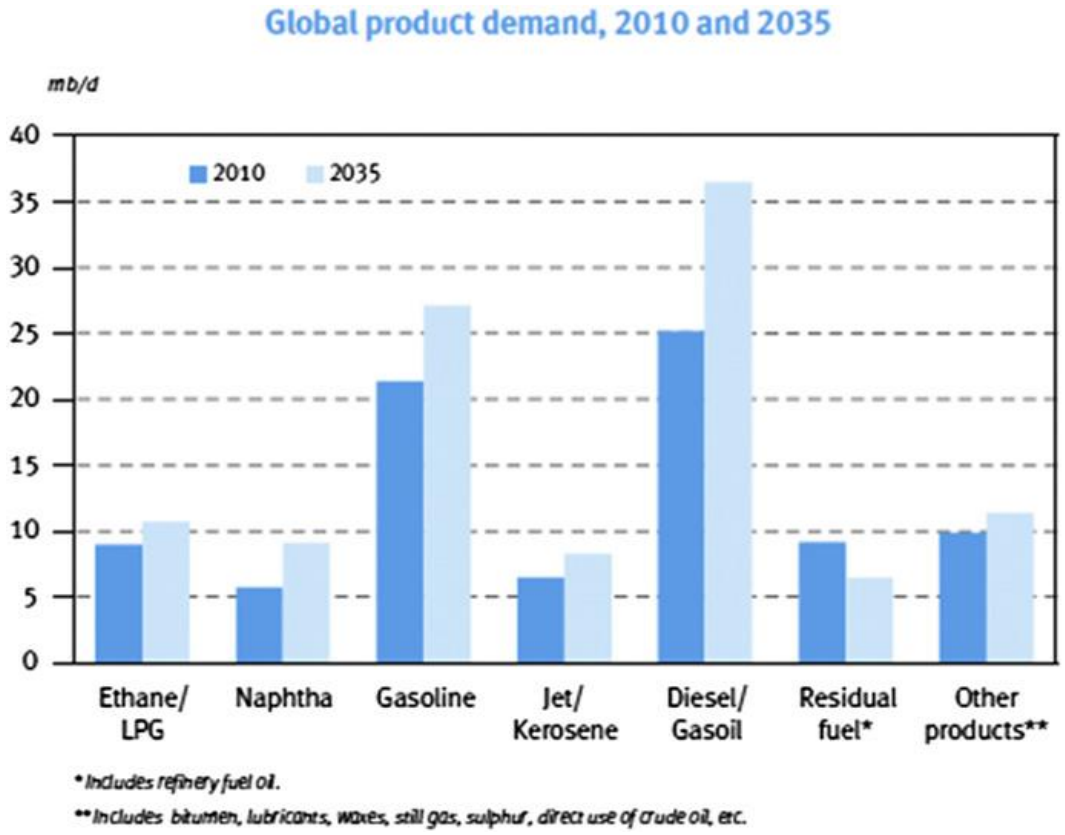

Fig. 3-11 Global product demand between 2010 and 2035 [33].

4 DME PRODUCTION

4.1 Direct DME Production

Direct DME production process consists of pretreatment, reforming, gas cleaning-recycles, DME synthesis, and separation and purification of DME sections (**Fig 4-1**).

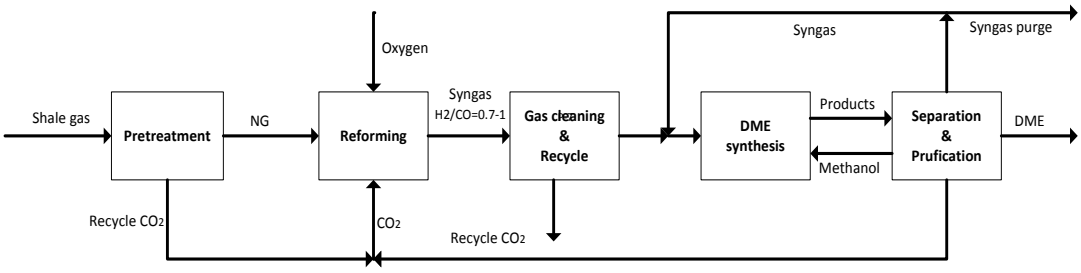

Fig. 4-1 Simplified block diagram of the direct dimethyl ether production.

4.1.1 Pretreatment Section

The first step of the production of DME from shale gas is the purification of shale gas. As shown in **Fig.4-2**, shale gas is first sent to acid-gas removal unit and then dehydration process follow the first step.

The nitrogen removal unit is the next step that is membrane separation process. In this process (**Fig.4-3**), two streams are produced that are nitrogen-rich stream to fuel and nitrogen-reduced stream for later production process. The cooled nitrogen-reduced stream is sent to de-methanizer and then de-ethanizer to recover natural gas liquids.

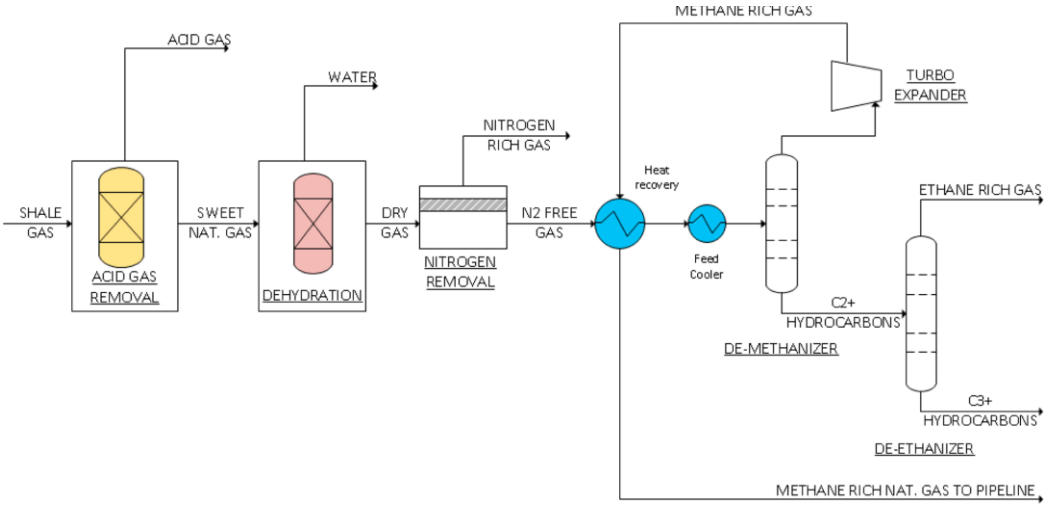

Fig. 4-2 General gas processing flow diagram [1].

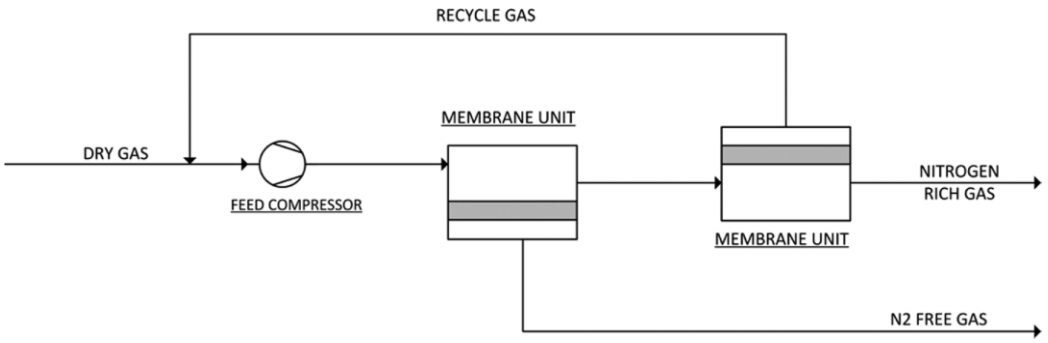

Fig. 4-3 Nitrogen removal process [1].

4.1.2 Reforming Section

The second section is called reforming. In this unit, gasification process occurs that converts the methane to syngas (mixture of CO and H_2). In general, the range for gasification process is between 800 °C to 1800 °C. However, type of feedstock and gasifier determines the exact temperature of process [41]. The detailed information of reforming types can be found in **Section 3.2.1.**

Dry reforming of methane was selected as a reforming type for direct production method. In order to produce DME from syngas directly, the ratio of H_2: CO should be between 0.7 and 1. Thus, dry reforming provides the necessary ratio during reformer reactions. Dry reforming is getting special attention due to environmental problems. Thanks to dry reforming, CO_2 can be converted to valuable syngas by reacting methane. However, the dry reforming of methane is thermodynamically unfavorable since methane and CO_2 are stable molecules. High reaction temperature is required for formation of syngas. There are many studies and they have showed increase recently to demonstrate the applicability of dry reforming. As a result, there are some methods for dry reforming such as plasma methods and catalytic methods [42]. In general, supported noble metals (Pt, Pd, Rh, Ru) and non-noble transition metals (Ni, Co, Fe) are the two categorized groups of catalysts that are used for dry reforming of methane [43].

4.1.3 DME Synthesis Section

The reaction conditions in direct synthesis DME reactor are 240-280 °C and 30-70 bars. General reactor conditions are represented in **Table 4-1**. The overall reaction is

exothermic, so the equilibrium of reaction is favored by low temperatures and high pressure. Three reactions occur simultaneously in reactor to produce DME from syngas:

Methanol synthesis:

$$CO + 2H_2 \leftrightarrow CH_3OH \qquad \Delta H = -91 \text{ kJ/mol} \qquad (4\text{-}1)$$

Methanol dehydration:

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \quad \Delta H = -23 \text{ kJ/mol} \qquad (4\text{-}2)$$

Water-gas shift reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H = -41 \text{ kJ/mol} \qquad (4\text{-}3)$$

Overall reaction:

$$3CO + 3H_2 \leftrightarrow CH_3OCH_3 + CO_2 \quad \Delta H = -246 \text{ kJ/mol} \qquad (4\text{-}4)$$

The first reaction is the methanol synthesis reaction. Carbon monoxide and hydrogen gives a reaction to produce methanol. As a second reaction, the methanol dehydration occurs, and two moles methanol reacts to produce one mole dimethyl ether and one mole water. The third reaction is water gas shift reaction that produces carbon dioxide and hydrogen. As an overall reaction, three moles carbon monoxide and three moles hydrogen reacts to produce one mole dimethyl ether and one moles carbon monoxide.

Table 4-1 Syngas to DME process conditions.

Syngas to DME	**Conditions**
Temperature (°C)	240 – 280
Pressure (bar)	30 – 70
H_2 : CO ratio	0.7 – 1
Catalysts	Cu–ZnO–Al_2O_3/HZSM-5
Reactor types	Fluidized-Bed, slurry phase, fixed bed reactors

The methanol synthesis and water-gas shift reaction are catalyzed by Cu–ZnO–Al_2O_3. On the other hand, the methanol dehydration reaction is catalyzed by an acidic catalyst (HZSM-5) [44].

Fluidized-bed, slurry phase and fixed bed reactors can be used for direct DME production. The slurry phase reactor was proposed for direct production by Air Product and Chemicals in 1991[45]. Later, the fixed-bed reactor and fluidized-bed reactor were proposed as an ideal reactor. Compared these reactor types, the gas–solid mass transfer resistance in a fluidized-bed reactor is smaller than the slurry-phase and fixed-bed. The reaction of DME is highly exothermic. Thus, the remove of heat and the control of temperature are very important in reactor. In fluidized-bed reactor, excellent temperature control is achieved due to the successful mixing of catalyst particles in the bed [44].

4.1.4 Separation, Purification and Recycle Sections

The fundamental of this section is to separate CO_2 by following reformer, and to send this recycle CO_2 through reformer. There are three locations in system for recycle CO_2. The first comes from acid gas removal unit, the second recycle CO_2 is obtained after reforming process and the third one is the recycle CO_2 produced in DME reactor. In system, these three streams are combined and sent reformer to give reaction with CH_4 for syngas production.

Absorption, adsorption, cryogenic and membrane systems are the common technologies for CO_2 separation. The selection of technology depends on the percentage of CO_2 in the feed composition, the conditions of feed such as pressure and temperature, the product purity and the final destination of the product. All technologies have advantages and disadvantages. The advantages of absorption are recycling of sorbent and non-dependence on operator. On the other hand, oxygen causes corrosion on carbon steel facilities and the degradation of the solvent due to NOx and SOx is the another problem. Recycling of sorbent and high operating flexibility are the advantages of adsorption. Adsorption technology is not able to deal high concentration of CO_2 and smaller gases can be adsorbed. Another technology is the cryogenic that does not need absorbent and operates on atmospheric pressure. However, several steps are required to remove water and this increase the cost of process [46, 47].

Membrane systems are the promising candidate on the traditional separation processes. Especially, it is convenient for streams that contain more than 15% of CO_2 and comes from steel production plant. No moving parts and modularity are needed for

the membrane systems and the system is able to give instantaneous respond to the variations [46, 47].

Another issue is the separation of unreacted syngas from reactor yield. Unreacted syngas stream is divided two streams of to-fuel and recycle to DME reactor. The mixture of DME, methanol and water is sent to first column of DME distillation and DME is distillated. In second column of methanol distillation, distillated methanol is sent through to DME reactor as recycle to react. **Fig. 4-4** shows the direct synthesis route.

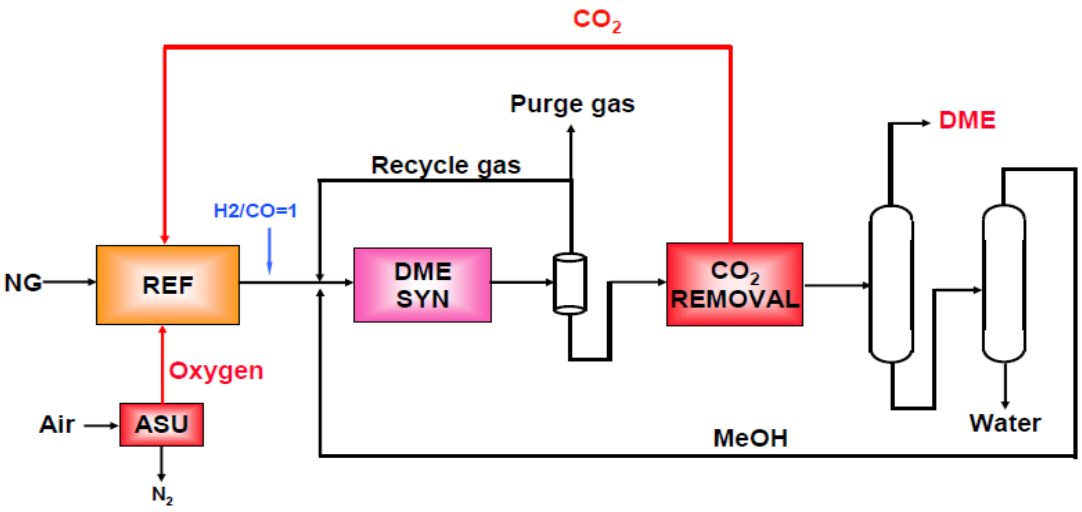

Fig. 4-4 Direct synthesis route (© 2005 TOYO Engineering Corporation).

4.2 Indirect DME Production

There are seven main sections to produce DME from shale gas by indirect method (methanol-to-DME). These steps are pretreatment, reforming, gas cleaning, methanol synthesis, separation1, DME synthesis and separation2 (**Fig. 4-5**).

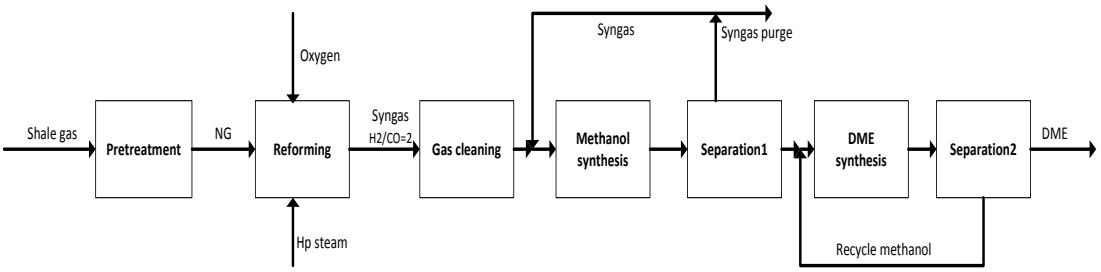

Fig. 4-5 Simplified block diagram of the indirect dimethyl ether production.

4.2.1 Pretreatment Section

In this section, the same processes are carried out as the direct production. The detailed information can be found in **Section 4.1.1.**

4.2.2 Reforming Section

In reforming section of indirect method, the partial oxidation of methane was used as a reforming type. For indirect method, the required H_2: CO ratio is 2:1. The syngas can be produce with a H_2/CO ratio of about 2 to 1.7. Thus, after partial oxidation reforming, the water-gas shift reaction is needed to reach the 2:1 ratio of syngas.

The operation conditions for the oxidation are between 1300 to 1500°C and up to 70 bar. The carbon efficiency of process exceeds of 95% and methane slip of process is

approximately 1%. The produced syngas comprises almost 95% H_2 and CO. The remaining 5% is H_2O, CO_2, N_2 and traces of hydrocarbons and nitrogen compounds. The partial oxidation can be catalytic and non-catalytic [48].

4.2.3 Methanol Synthesis Section

Methanol is the one of the most important organic chemical because many other chemicals can be produced from methanol. Methanol is produced generally from syngas by catalytic reaction. The equilibrium of methanol reaction is favored by low temperatures and high pressure. The optimum conditions for methanol reactor are 50-100 atm and 200-280 °C (**Table 4-2**). During methanol production, two types of reaction occur in reactor. First reaction is between water and carbon monoxide and second reaction is between carbon dioxide and hydrogen. As a result of these two reactions, one mole methanol is generated for one mole of carbon monoxide and two moles of hydrogen.

Table 4-2 Syngas to methanol process conditions.

Syngas to methanol	**Conditions**
Temperature (°C)	200 – 280
Pressure (atm)	50 – 100
H2 : CO ratio	2
Catalysts	$CuO/ZnO/Al_2O_3$
Reactor types	Single or Multi-fixed bed adiabatic reactor
	Tubular, isothermal reactors

The reactions are occurring in reactor;

$$CO\ (g) + H_2O\ (g) \leftrightarrow H_2\ (g) + CO_2\ (g) \qquad \Delta H = -41\ kJ/mol \qquad (4\text{-}5)$$

$$CO_2\ (g) + 3H_2\ (g) \leftrightarrow CH_3OH\ (l) + H_2O\ (g) \qquad \Delta H = -50\ kJ/mol \qquad (4\text{-}6)$$

Overall reaction:

$$CO\ (g) + 2H_2\ (g) \leftrightarrow CH_3OH(l) \qquad \Delta H = -91\ kJ/mol \qquad (4\text{-}7)$$

The catalyst is the most important part of methanol synthesis because it can be poisoned by small amounts of sulfur or chlorine compounds. Thus, the high level of attention to catalyst is required in order to maintain high activity and selectivity of catalyst. The reaction of methanol is exothermic and the heat should be removed to increase the conversion [49].

4.2.4 DME Synthesis Section

The dehydration of methanol is an exothermic and equilibrium reaction. The optimum reaction conditions for reactor are 220-280 °C and 10-20 atm (**Table 4-3**).

Table 4-3 Methanol to DME process conditions.

Methanol to DME	**Conditions**
Temperature (°C)	220 – 280
Pressure (atm)	10 – 20
Catalysts	Solid acid catalysts and alumina
Reactor types	Adiabatic bed, fixed-bed

Methanol dehydration:

$$2\ CH_3OH \leftrightarrow CH_3\text{-}O\text{-}CH_3 + H_2O \quad \Delta H = -23.4\ kJ/mol \qquad (4\text{-}8)$$

Silica alumina, γ-alumina, the conventional bimolecular catalysts and different kinds of zeolites can be used for methanol dehydration [50].

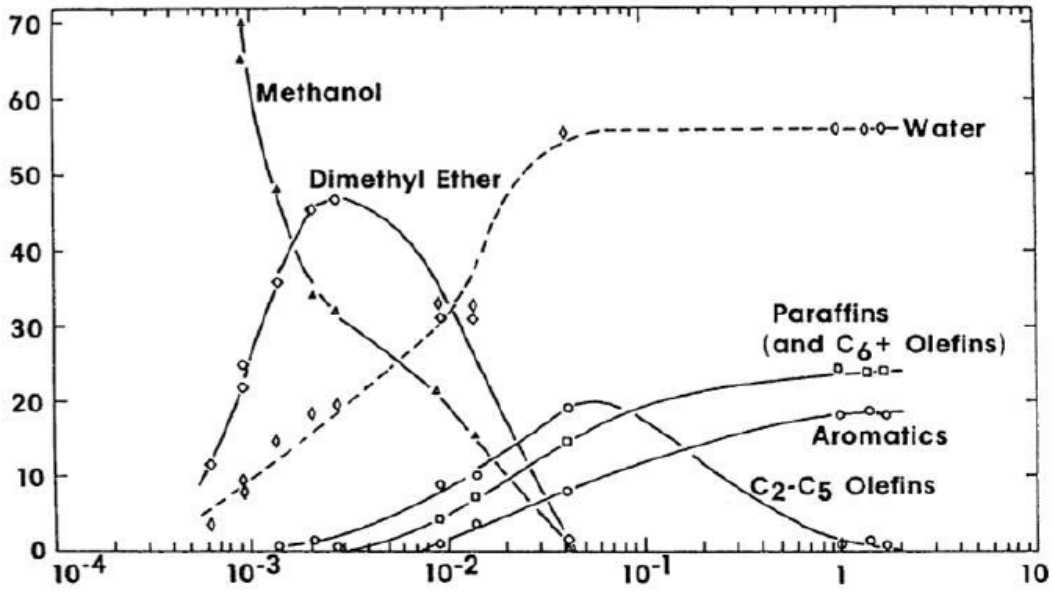

Fig. 4-6 Product time plot of products in *w/w* % against space time in hours [49].

4.2.5 Separation, Purification and Recycle Sections

Following the syngas production process, CO_2 is separated from syngas and CO_2 syngas is sent to methanol reactor to produce methanol from syngas.

After methanol reactor, the unreached syngas is separated and divided two streams that are through to methanol reactor as recycle and to-fuel. Then, a crude methanol is sent through DME reactor. In separation2 section, the mixture of DME

reactor product goes DME distillation column to separate DME from mixture, then methanol is distillated in methanol column. Distillated methanol is sent DME reactor again. Indirect synthesis route is shown in **Fig. 4-7**.

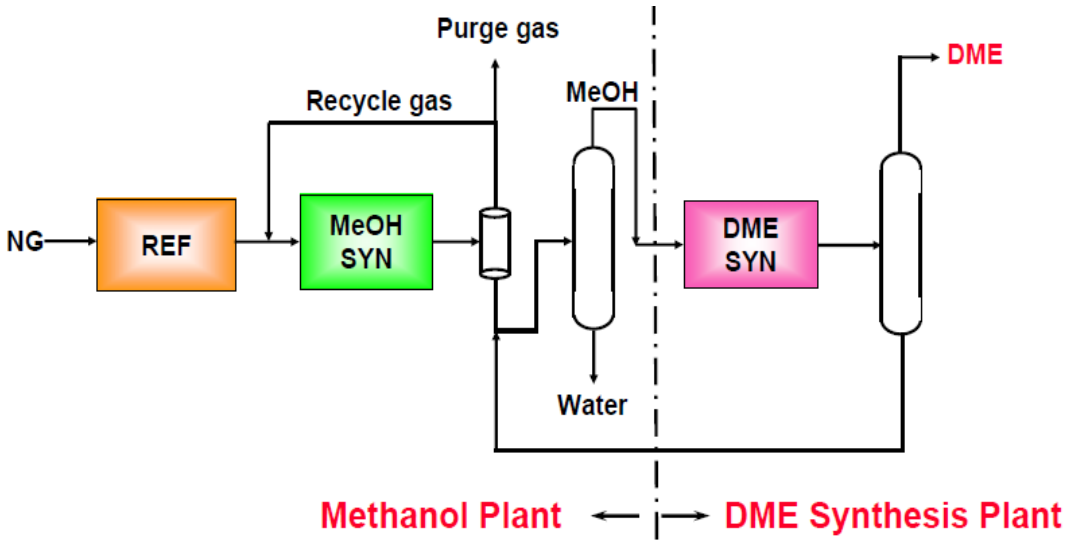

Fig. 4-7 Indirect synthesis route (© 2005 TOYO Engineering Corporation).

5 METHODOLOGY

Indirect and direct process simulation of commercial DME plant was carried out by Aspen Plus. H_2, O_2, N_2, H_2O, CH_4, CO, CO_2, C_2H_6, C_3H_8, butanol, methanol and DME are the components for simulation. RGIBBS thermodynamic equilibrium model of ASPEN Plus simulation was used to model all reformers, methanol reactor and direct DME reactor. RSTOIC model ASPEN Plus was used to model methanol dehydration reactor.

The Barnett shale gas was selected as a shale gas source in order to use in process and the composition of different wells in Barnett play can be found in **Table 1-3.** The composition of well-1 was used in simulation. Target capacity of 3250 ton per day was selected for both plants. The direct production method was designed as five main sections. However, the design of indirect production method consisted of seven main sections. In the direct method, the combination of partial oxidation and dry reforming was applied in reformer to reach syngas ratio of 0.7 – 1. On the other hand, the combination of partial oxidation and water-gas shift reaction was used in indirect method to produce syngas that has the ratio of 2:1.

To maximize the energy recovery, the energy integration was applied on process. In order to perform techno-economic analysis of both methods, the capital costs of plants were estimated and operating costs were calculated based on the simulation results and literature. The fixed capital cost, operating cost, return of investment, CO_2 and water production were taken as criteria to compare two methods.

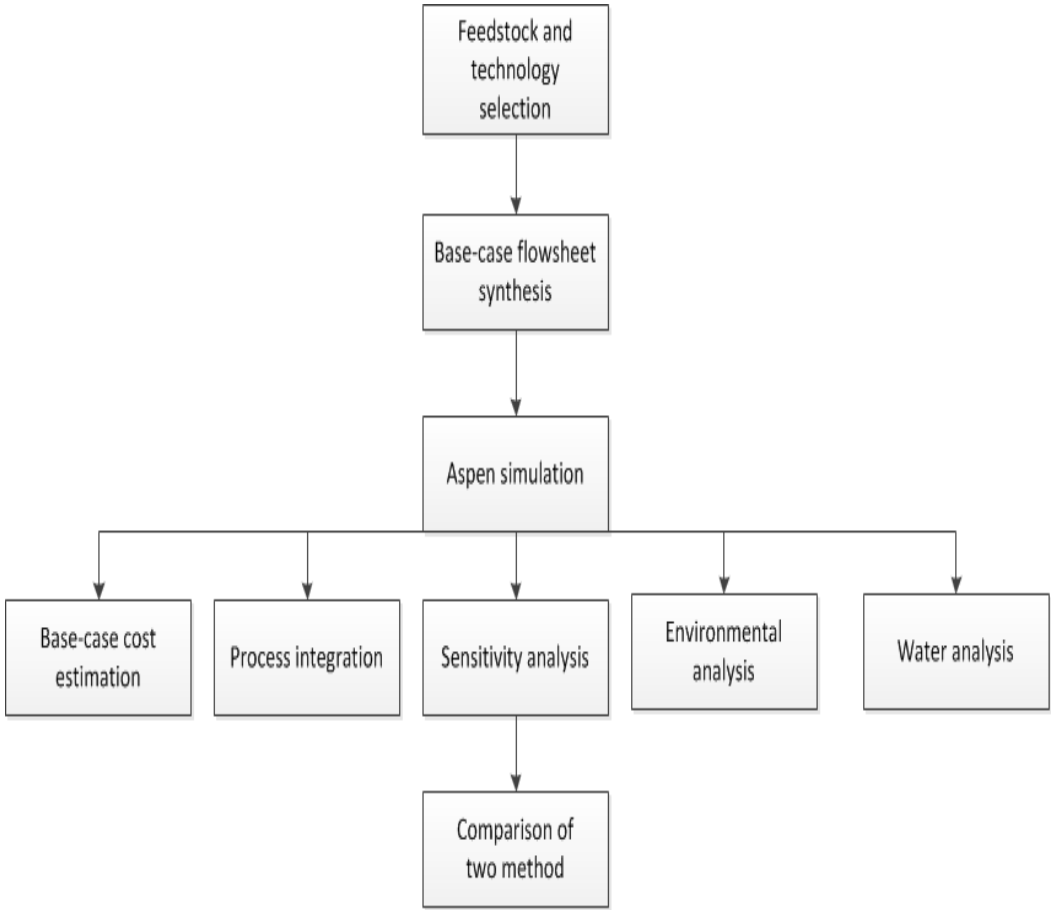

Fig. 5-1 Scope of project.

6 RESULTS AND DISCUSSION

6.1 Process Synthesis of the Direct Method

In order to reach pipeline standards, the shale gas feedstock is first needed to undergo several pretreatment steps due to contaminations. In pretreatment section, the shale gas is sent through acid gas removal and nitrogen gas separation units, respectively [1]. The carbon dioxide is separated at 39 atm. After acid gas removal unit, carbon dioxide free shale gas stream is separated into a reduced nitrogen-reduced stream and a nitrogen-rich stream in nitrogen removal unit by using membrane separation process.

The nitrogen-reduced stream is cooled and sent through the de-methanizer column to separate methane from the higher boiling hydrocarbons. The de-ethanizer column is the last unit theoretical stages. On the other hand, the de-methanizer is designed as 15 theoretical stages.

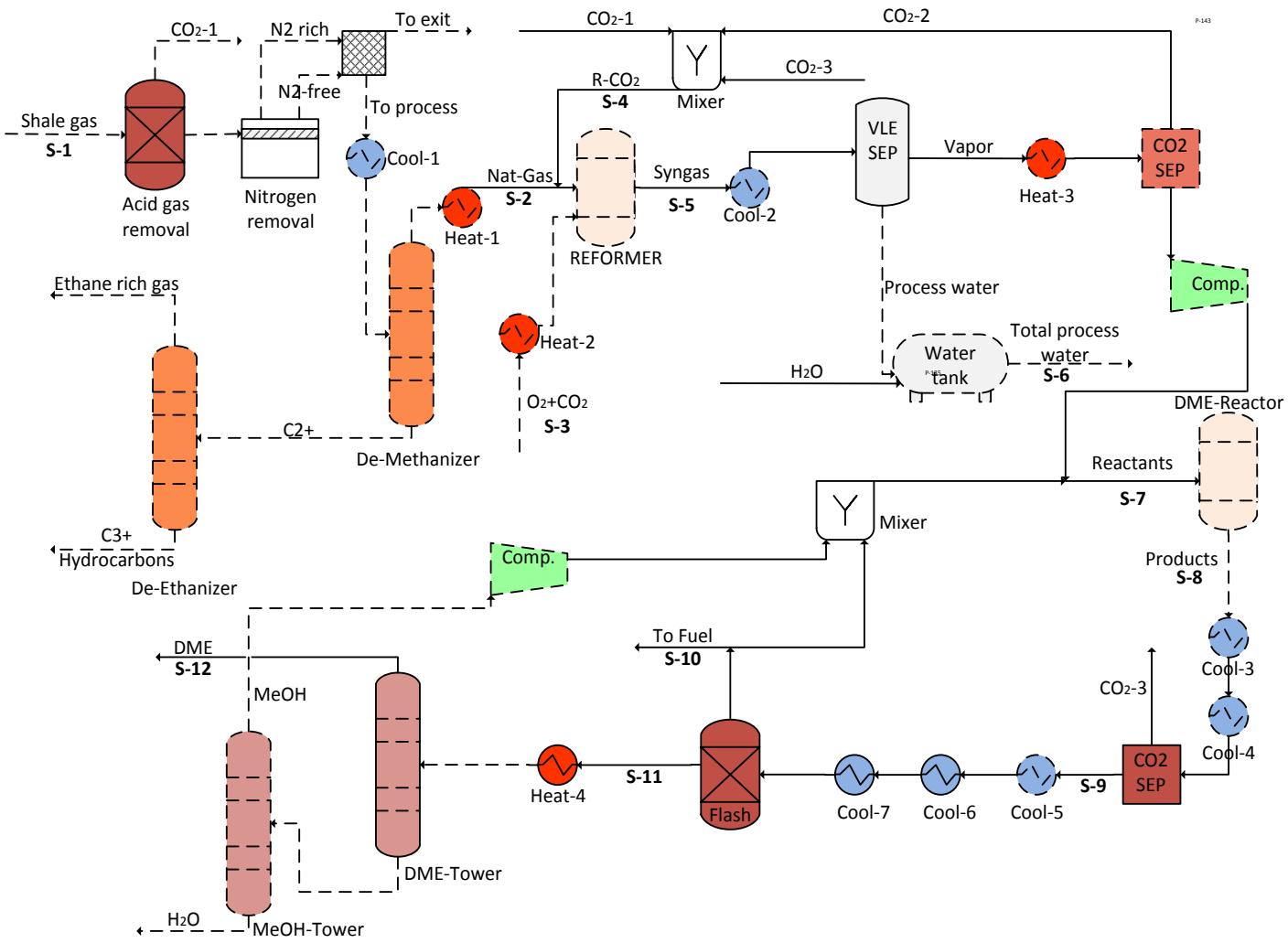

Fig. 6-1 Overall process flowsheet of the direct production method.

The reforming of methane is the next section to produce syngas (mixture of CO and H_2). Detailed information about reforming types can be found previous sections. Process objectives, availability of material, energy resources, final product, energy requirement, environmental issues and safety issues are the main concepts for the selection of reforming type or types [34]. The dry reforming of methane was selected for direct production method in order to provide the ratio of H_2: CO between 0.7 and 1 that is the required DME production from syngas. Nowadays, the capture and transformation of CO_2 to other chemicals and chemicals hold important place in research world due to its environmental impacts such as greenhouse problem. Therefore, the CO_2 reforming of methane has been getting significant attention and also the applicability of this reforming by using Pt group metals has been demonstrated by researchers [51].

The mixture of CO_2 and O_2 (the percentage of CO_2 is %85-90) is heated 472 K and sent through reformer. At the same time, the pipeline natural gas and recycle CO_2 are fed to the reformer. During process, the recycle CO_2 is come from three sources. The first one is from pretreatment section (CO_2-1), the second is the separation of CO_2 following the reformer (CO_2-2) and the last one is the separation of CO_2 after DME reactor (CO_2-3). As result of reactions, the reformer produces the syngas which has the ratio of H2: CO between 0.7 and 1.

Table 6-1 Key streams data of the direct production method.

component	units	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9	S-10	S-11	S-12
hydrogen	lbmol/h	0	0	0	0	20457	1.3	21204.1	1500	1500	747.340	5.96	5.96
water	lbmol/h	0	0	0	0	1649.23	1553.6	122.7	27	27	0.0001	27	0
methane	lbmol/h	12220	11120.2	0	0	66.64	0.2148	105	97.5	97.5	38.84	19.8	19.8
nitrogen	lbmol/h	1202.27	10	0	0	10	0.0127	18.55	18.55	18.55	8.58	1.4	1.4
ethane	lbmol/h	1232.7	0	0	0	0	0	0	0	0	0	0	0
propane	lbmol/h	350	0	0	0	0	0	0	0	0	0	0	0
carbon mon.	lbmol/h	0	0	0	0	22540	20	24738	4843	4843	2223.54	396	396
methanol	lbmol/h	0	0	0	0	0	0.0019	0.003	113	113	0.0872	112.8	0
butanol	lbmol/h	0	0	0	0	0	0	0	0	0	0	0	0
dimethyl-ether	lbmol/h	0	0	0	0	0	0	0	6712.6	6712.6	106.71	6500	6498
acetone	lbmol/h	0	0	0	0	0	0	0	0	0	0	0	0
oxygen	lbmol/h	0	0	611	0	0	0	0	0	0	0	0	0
carbon dioxide	lbmol/h	213	0	4582.5	7640.75	742.6	7.6	0	6692.4	0	0	0	0
total flow	lbmol/h	15218	11130	5193.4	7640.75	45460	1582.6	46407.7	20004	13312	3124.8	7062.3	6804.2
total flow	lb/h	291597	178672	221228	336258	736190	28886.5	748670	748670	454123	69569.5	314983	310817
temperature	°F	104	78.8	78.8	273.4	2192	-	500	500	278	14	14	112
pressure	psia	573	203	377	377	203	-	797	797	797	725	725	154

As a fourth section of process, the syngas is first cooled 313 K and sent through a flash column (VLE-SEP) to remove water from syngas. Then, CO_2 is separated from syngas and this stream is compressed to 55 atm and sent to the DME reactor where it reacts at 533 K. The detailed information of direct DME production reactor is given in 4.1.3.

RGIBBS thermodynamic equilibrium model of ASPEN Plus simulation is used to model DME reactor. During reaction between carbon monoxide and hydrogen, significant amount of CO_2 is produced in reactor. After reactor, the product stream is cooled and sent through the CO_2 separation unit. CO_2 is removed from products and the product stream is sent through another section to separate unreacted syngas from products. Unreacted syngas is divided two streams. First one is to fuel and second one is sent again DME reactor as a recycle.

Lastly, the product stream is cooled and the stream visits DME and MEOH towers, respectively. DME is separated in DME-Tower as a final product and the unreacted methanol is removed from liquid water in MEOH-Tower and sent though DME reactor as a recycle by combining the unreacted syngas. The DME and MEOH columns were designed as 20 theoretical stages and feed tray locations are 11. Overall process flowsheet of the direct production method can be found in **Fig. 6-1** and key streams data of the direct production method can be found in **Table 6-1**.

6.2 Process Synthesis of the Indirect Method

Similar to the direct production, the indirect production process starts with a pretreatment section that is formed of same procedure as the direct production. Unlike

the direct way, partial oxidation of methane was selected to produce syngas. The reaction between methane and oxygen is exothermic and gives theoretically a ratio of 2:1 (H_2: CO).

First, the oxygen stream is heated to 473 K, and the heated oxygen and the pipeline natural gas are sent to partial oxidation reactor. The reaction occurs at 19.7 atm to produce syngas that has approximately a 1.8:1 ratio of H_2: CO contrast to the theoretical ratio. Then the syngas stream is sent through a flash column to separate liquid water and then to the water−gas shift (WGS) reactor in order to adjust the ratio to the stoichiometric value of 2.0. The reaction in WGS reactor occurs at 573 K.

As a next step, the new syngas stream is cooled and sent to another flash column to separate liquid water. Then, CO_2 is removed from syngas in separation unit and the stream is compressed to 75 atm in order to be sent MEOH reactor where it reacts at 513 K. The equilibrium of methanol reaction is favored by low temperatures and high pressure.

Like to the DME reactor for direct production, the methanol reactor was modeled by using the RGIBBS thermodynamic equilibrium model of ASPEN Plus simulation. After the methanol reactor, the product stream is cooled and the unreacted syngas is removed, respectively. The unreacted syngas is divided two streams as a to-fuel and recycle through the methanol reactor.

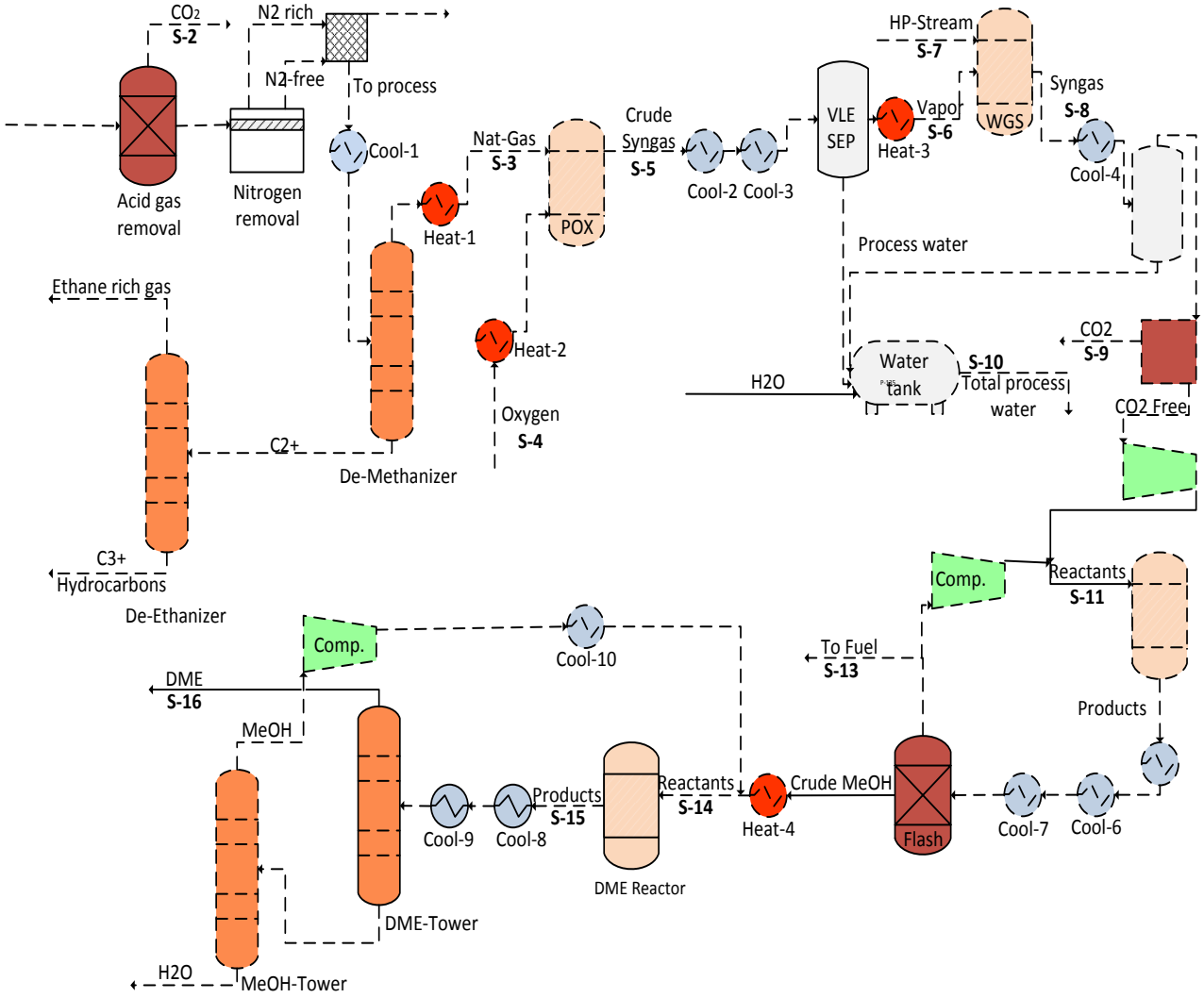

Fig. 6-2 Overall process flowsheet of the indirect production method.

Table 6-2 Key streams data of the indirect production method.

component	units	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9	S-10	S-11	S-12	S-14	S-16
hydrogen	lbmol/h	0	0	0	0	27227	27221	0	28110	0	6.1	30501	4834.4	52.41	52.41
water	lbmol/h	0	0	0	0	3472	78.22	855	100.9	0	9844	79.04	01.58	17.08	0
methane	lbmol/h	16224	0	15411	0	61.4	60.92	0	33	0	0.6875	44.62	33	8.268	8.268
nitrogen	lbmol/h	1596.2	0	13.25	0	13.25	13.25	0	13.2	0	0.0587	23.6	23.6	2.84	2.84
ethane	lbmol/h	1638	0	0	0	0	0	0	0	0	0	0	0	0	0
propane	lbmol/h	465	0	0	0	0	0	0	0	0	0	0	0	0	0
carbon mon.	lbmol/h	0	0	0	0	14670	14626	0	13851	0	63.02	14555	1616.1	206.45	206.45
methanol	lbmol/h	0	0	0	0	0	0	0	0	0	7.06	18.1	12903	16069	3.98
butanol	lbmol/h	0	0	0	0	0	0	0	0	0	0	0	0	0	0
dimethyl-ether	lbmol/h	0	0	0	0	0	0	0	0	0	0	0	0.5	0.35	6427.7
acetone	lbmol/h	0	0	0	0	0	0	0	0	0	0	0	0	0	0
oxygen	lbmol/h	0	0	0	9750	0	0	0	0	0	0	0	0	0	0
carbon dioxide	lbmol/h	286	286	0	0	678.8	655.4	0	1459	1459	23.8	15.8	82	50.4	50.4
total flow	lbmol/h	20208	286	15424	9750	42123	42654	855	43566	1459	9923	69596	19499	16407	6752.2
total flow	lb/h	387290	12587	247605	311968	559592	496139	15399	511537	64193	179908	728080	473252	523510	302525
temperature	°F	104	104	78.8	78.8	2327	572	482	617	104	-	254.3	392	500	113.1
pressure	psia	573	573	377	377	362	573	573	573	573	-	1103	1103	263	154

The crude methanol stream is heated to 533 K and sent through DME reactor. The reaction occurs at 18 atm to produce DME from methanol. The conversion of methanol is 75-80% and then the unconverted methanol is separated in MEOH column, and the recycle MEOH stream is compressed, cooled and sent to DME reactor to react. Before the MEOH column, the final product of DME is distillated in DME column. The dehydration of methanol is an exothermic and equilibrium reaction. **Fig. 6-2** shows overall process flowsheet of the indirect dimethyl production and **Table 6-2** key streams data of the indirect production method.

6.3 Economic Analysis

The fixed capital investment (FCI) for both the direct and indirect plants were estimated by using the six-tenths factor rule based on the cost of a 3250 ton/day DME plants. While FCI for the direct method was estimated $MM 1050, it was estimated $MM 1400 for the indirect method [1, 52, 53, 54].

Based on the simulation streams results, the operational cost estimations were carried out and the economic data is shown in **Table 6.3** for base case design.

Based on the economic data, the direct production method has significant advantage on the indirect production method. The consumption of shale gas is almost 28% less than the indirect method during process. In order to produce 3250 ton/day DME, approximately 5000 ton/day methanol production is required for indirect production. Thus, the shale gas consumption difference occurs between two methods.

Table 6-3 Key economic results for base case design.

item	Rate			unit cost	annual cost ($MM/yr)	
	direct	indirect			direct	indirect
pipeline quality shale gas	100.5	139.27	MMSCF/d	$4.50/kSCF (or/MMBtu)	149.26	206.81
oxygen	19,079	311,988	lb/h	$0.05/lb	11.91	123.5
CO2	214,500	-	lb/h	$0.01/lb	17.979	-
heating utility	164.45	456.63	MMBtu/h	$4.00/MMBtu	5.2	14.46
cooling utility	915.66	1545	MMBtu/h	$1.94/MMBtu	14	23.744
power consumption	21,790	19,154	kW	$0.05/kWh	8.632	7.6
waste treatment	35.1	1928.55	ton/d	$0.48/ton	0.0056	0.3055
labor					3.80	3.80
DME sales	3250		ton/d	$900/ton (2.26/gal)	965.25	965.25

Especially, the consumption of oxygen creates significant difference between two methods due to main reforming types. The main reforming type of the indirect production is partial oxidation, so the feed of oxygen ratio between indirect and direct is approximately 16.35 per hour. Also, the utility consumption of the direct method in terms of heating and cooling is less than the indirect method. However, the water production of the indirect method is much more compared to the direct method.

Pretreatment cost estimations of the both processes were performed based on the streams result from separations of CO_2, nitrogen, C_2 and C_3 (**Table 6-4**). As expected, the required cost for indirect method is higher than direct since the flow of shale gas is higher in indirect production.

Table 6-4 Pretreatment cost estimation.

	flow rate (lb mol/h)		total annualized cost ($MM/yr)	
	direct	**indirect**	**direct**	**indirect**
acid gas removal	15217.8	20207.85	17.06	22.65
N2 removal	15217.8	20207.85	59.462	78.96
C2 credit	1232.4	1636.7	23.56	31.3
C3 credit	349.7	464.75	28.21	37.5
total			24.752	32.81

6.4 Sensitivity Analysis

The sensitivity analyses of the both process were performed by consideration of changes in feedstock, product values and plant capacities. The working capital investment (WCI) was assumed to be 15% of TCI, the total capital investment (TCI=WCI+FCI)), 330 operating days, a tax rate of 30 and a ten-year linear depreciation scheme (10% of the FCI) were used for calculations. The potential probability of the both process is evaluated by using the return on investment (ROI) [53, 55]. The ROI is shown by formula:

$$\text{ROI}=\frac{(annual\ revenues-\ annual\ operating\ cost-depreciation)x\ (1-tax\ rate)x0.7+depreciation}{TCI} \quad (6\text{-}1)$$

Fig. 6-3 represents the ROI of the both processes versus DME price ranging from $1.00 to $4.00 per gallon for natural gas prices of $2.00, $4.00, $6.00 and $6.00 per kSCF, respectively. By taking DME price as 2.26/gal and the natural gas price as $4.5/kSCF, the direct method is more attractive than the indirect method because the ROI of the direct method is 43.24% compared to the ROI of the indirect method (26%).

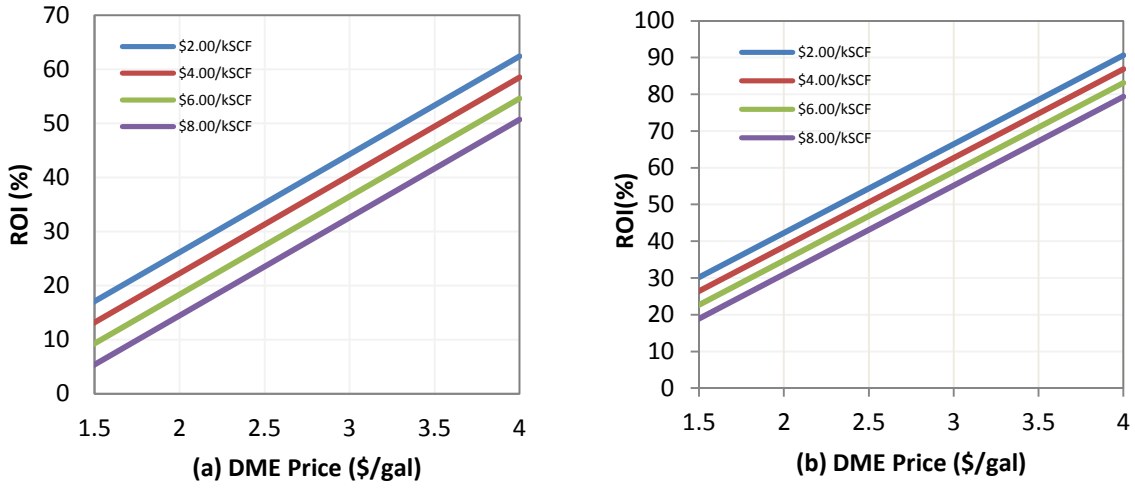

Fig. 6-3 Sensitivity analyses of the indirect (a) and direct (b) methods for ROI vs DME price (3250ton/d) at various price of shale gas.

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The ROI values of the both processes meet a required minimum ROI of 15%. However, the ROI of indirect method (12.78%) fall below the minimum value in case of $1.50/gal DME price. Even though the price of DME drops to $1.50/gal, the ROI of the indirect method (24.86%) keeps above the minimum requirement.

Fig. 6-4 and 6-5 show the effect of the plant capacity on ROI for different prices of DME and natural gas. As shown in **Fig. 6-4**, the increase of the plant capacity makes very close impact on ROI of the both processes for different shale gas prices. On the other hand, the impact of the plant capacity on ROI of the direct method is more attractive than the indirect method for different DME prices (**Fig. 6-5**)

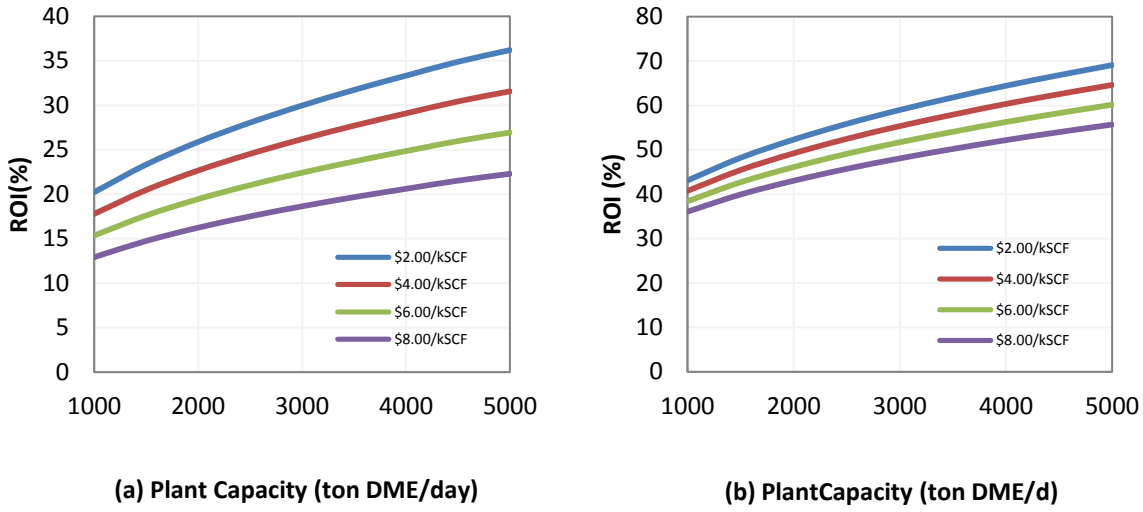

Fig. 6-4 Sensitivity analyses of the indirect (a) and direct (b) methods for ROI vs plant capacity at various price of shale gas.

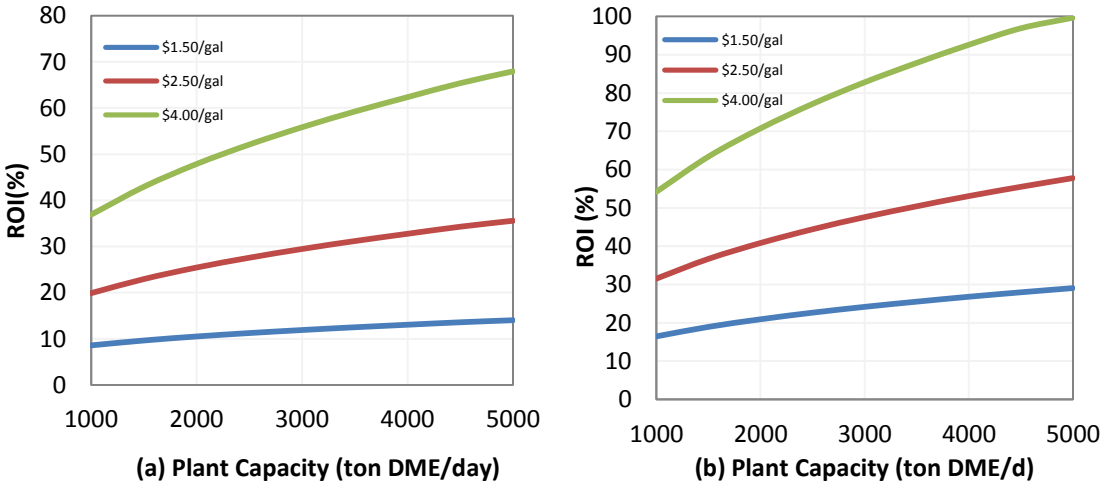

Fig. 6-5 Sensitivity analyses of the indirect (a) and direct (b) methods for ROI vs plant capacity at various price of DME**.**

6.5 Energy Integration of the Direct Production Method

Table 6-5 represents the heating and cooling duties of the process: (1) After acid gas and nitrogen removal, the shale gas is cooled via Cool-1. The natural gas stream is

heated in Heat-1, and the mixture of carbon dioxide and oxygen is heated (Heat-2) in order to send through reformer. Then, the syngas is cooled in Cool-2 to sent liquid water seperator and it is heated again in Heat-3 after seperation unit. The product stream of DME reactor is cooled via Cool-3,4 before the CO_2 seperation unit. Finally, the unreacted syngas is seperated and this stream is heated in Heat-4 and sent through DME column to get DME from the stream.

Table 6-5 Heat exchanger data of the direct DME process.

	Heat exchanger tag	**supply temperature (K)**	**target temperature (K)**	**heat duty (kW)**
H1	Heat-1	179	299	11,606.4
H2	Heat-2	299	473	4518.15
H3	Heat-3	313	410	15,678.78
H4	Heat-4	263	383	16,320.85
C1	Cool-1	313	230	-5848.7
C2	Cool-2	1473	313	-220,804.35
C3	Cool-3,4	533	410	-17,006
C4	Cool-5,6,7	410	300	-24,698

The heat integration was performed in order to reduce the operating cost. The thermal pinch analysis is applied among the hot and cold streams for heat integration. The table of exchangeable heat loads (TEHL) for direct process hot streams is shown in **Table 6-6** and the table of exchangeable heat loads (TEHL) for direct process cold

streams is shown in **Table 6-7**. The heat integration reduces minimum heating and cooling utilities to 0 and 221.2 MW (**Fig.6-8**). The cooling utility can be further reduced and electric power can be produced using cogeneration. After the combination of the heat and the power integrations, the energy integration's impact on the ROI of process is almost 2.25% (**Fig. 6-9**) [56].

Table 6-6 The table of exchangeable heat loads (TEHL) for direct process hot streams.

Interval	Load of H1 (kW)	Load of H2 (kW)	Load of H3 (kW)	Load of H4 (kW)	Total Load (kW)
1	-	-	-	-	-
2	-	-	-	-	-
3	-	-	1645	-	1645
4	-	901	144.3	-	1045.3
5	-	3424.2	548.34	-	3972.54
6	9520.55	11353.8	1818.18	-	22692.53
7	755.625	-	144.3	-	899.925
8	1148.55	-	219.4	-	1367.95
9	664.95	-	-	490.425	1155.375
10	4231.5	-	-	3011.8	7243.3
11	-	-	-	3711	3711
12	-	-	-	4410	4410

Table 6-7 The table of exchangeable heat loads (TEHL) for direct process cold streams.

Interval	Load of C1 (kW)	Load of C2 (kW)	Load of C3 (kW)	Load of C4 (kW)	Total Load (kW)
1	-	178926.5	-	-	178926.5
2	-	10363.6	7507	-	17870.6
3	-	12055.55	8732.75	-	20788.3
4	-	1057.5	766	-	1823.5
5	-	4018.4	-	4739.93	8758.33
6	-	13324.35	-	15716.61	29040.96
7	-	1057.5	-	1247.35	2304.85
8	596.7	-	-	1896	2492.7
9	345.8	-	-	1097.67	1443.47
10	2198.17	-	-	-	2198.17
11	2708.55	-	-	-	2708.55
12	-	-	-	-	-

Cascade and revised cascade diagrams for the direct production process can be found in **Fig. 6-6** and **Fig. 6-7**, respectively.

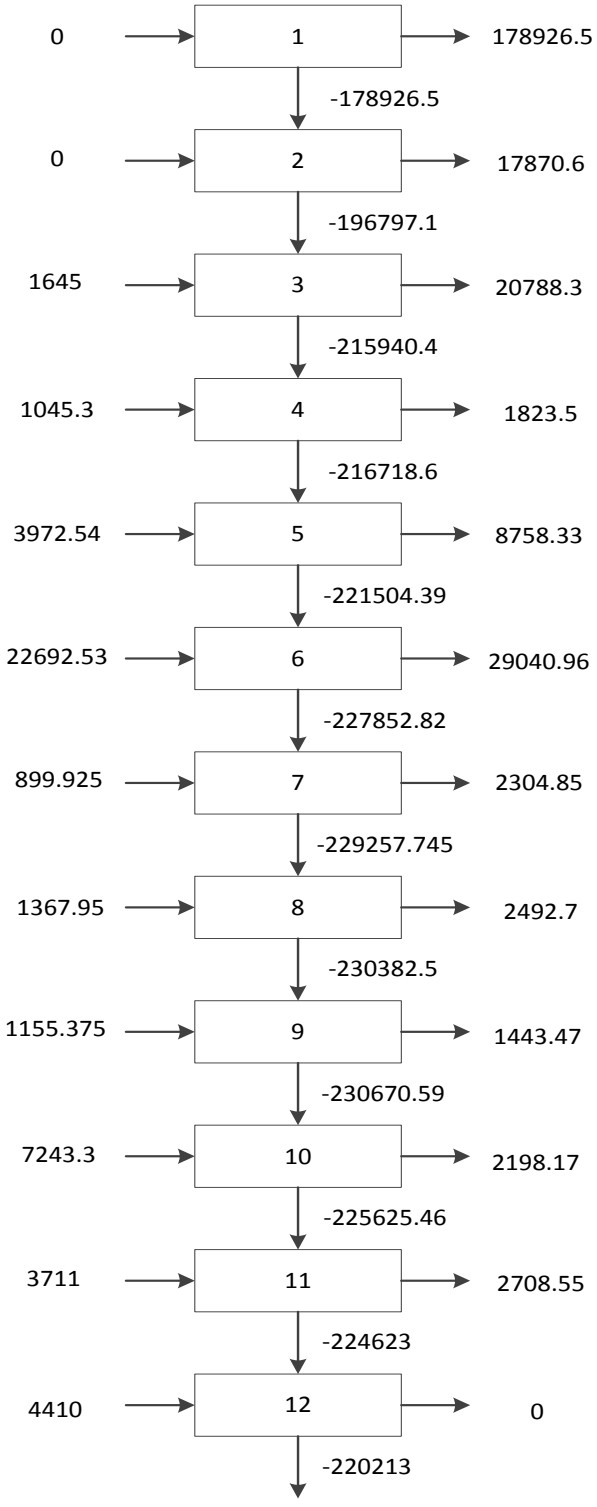

Fig. 6-6 Cascade diagram for the direct production process.

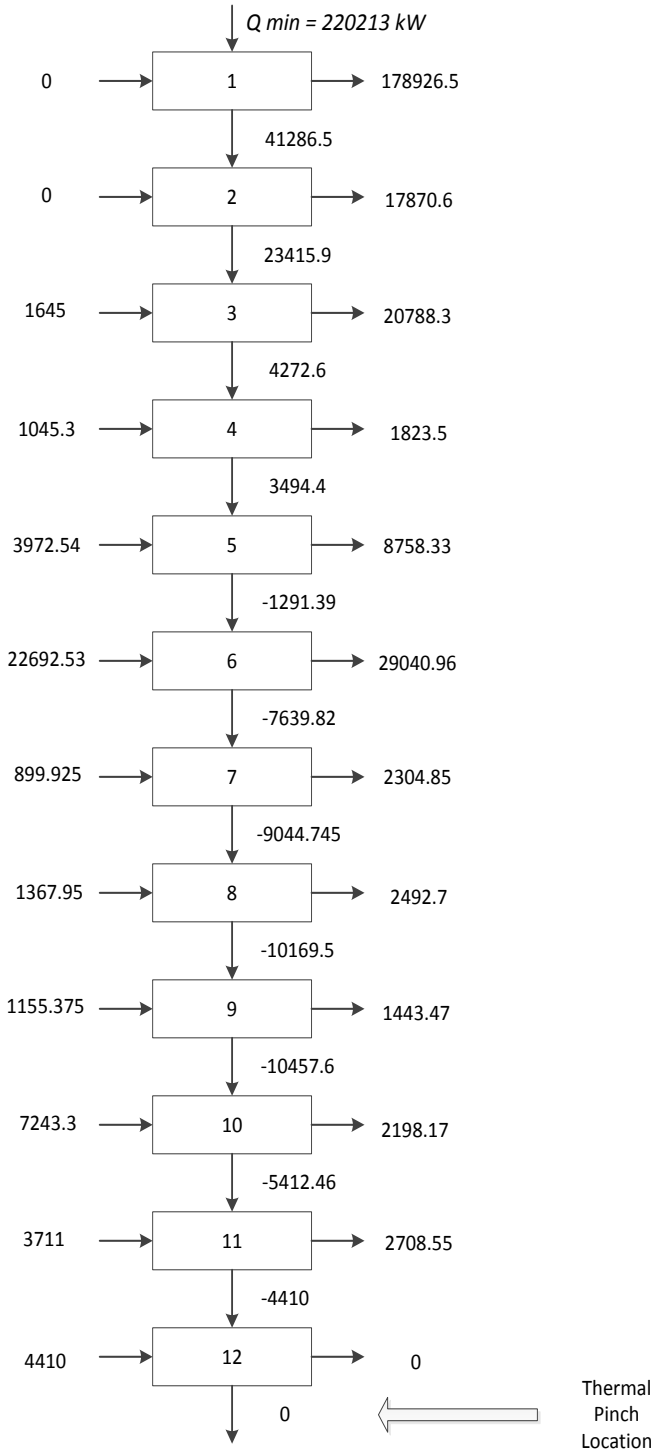

Fig. 6-7 Revised Cascade diagram for the direct production process.

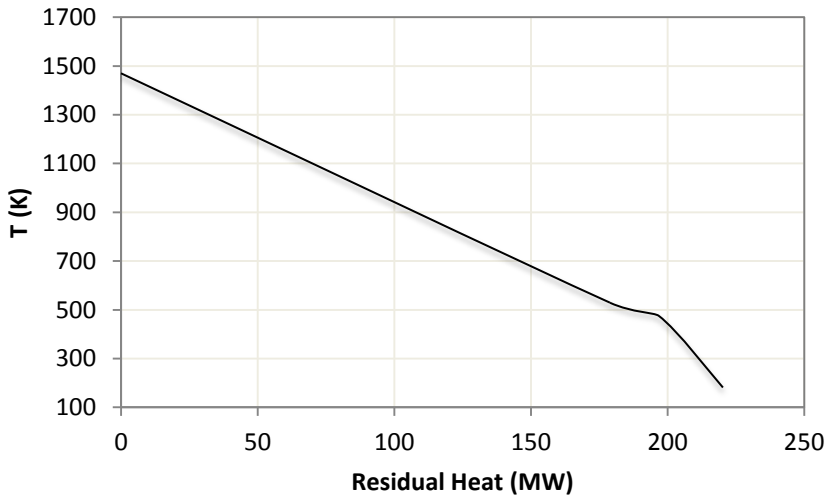

Fig. 6-8 Grand composite curve for heat integration of the direct process.

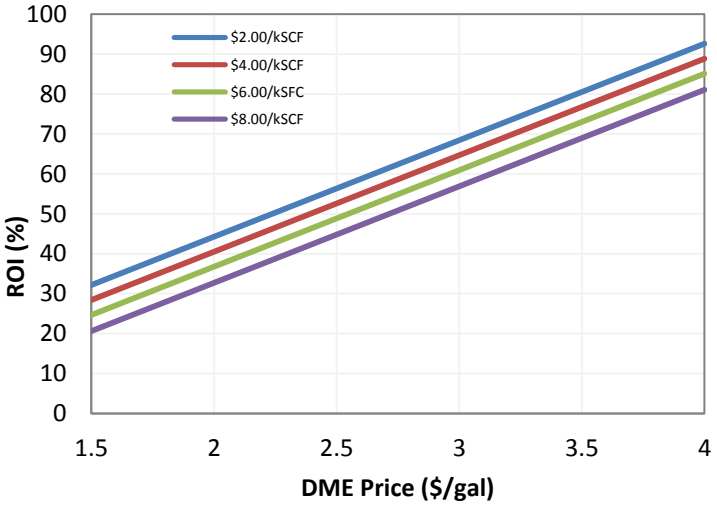

Fig. 6-9 Sensitivity analysis of the direct process after energy integration.

6.6 Energy Integration of the Indirect Production Method

Similar to the direct method, the indirect method has several heating and cooling duties. Following the acid gas and nitrogen removal sections, the she shale gas stream is cooled via Cool-1, and then natural gas and the oxygen streams are heated (Heat-1 and Heat-2) before entering POX reformer. The crude syngas is cooled (Cool-2, 3) and sent through the liquid separation unit. Then the stream is heated again (Heat-3) and sent through the WGS reactor. After methanol synthesis section, the product stream is cooled (Cool-5, 6, 7) and then the unreacted syngas is separated and heated (Heat-4) before entering the DME reactor. DME reactor products stream is cooled (Cool-8, 9) and sent through to DME tower to separate DME from product stream. Finally, recycle stream from MEOH tower is cooled and sent through the DME reactor again. **Table 6-8** represents heat exchanger data of the indirect DME process

Table 6-8 Heat exchanger data of the indirect DME process.

	Heat exchanger tag	supply temperature (K)	target temperature (K)	heat duty (kW)
H1	Heat-1	179	299	7973.55
H2	Heat-2	299	473	6410.95
H3	Heat-3	313	573	41,328.3
H4	Heat-4	318	533	78,115
C1	Cool-1	313	230	-6746.35
C2	Cool-2,3	1548	313	-249,054.65
C3	Cool-4	598	313	-46,812.35
C4	Cool-5,6,7	473	318	-75,823.15
C5	Cool-8,9	533	383	-70,207.15
C6	Cool-10	577	400	-4214

The heat and power integration were performed by using the same method in the direct method. As shown in **Fig.6-12**, the minimum heating and cooling utilities are 0 and 319 MW. The increment of the ROI for the indirect process is approximately 1.83% (**Fig. 6-13**). The table of exchangeable heat loads (TEHL) for indirect process hot streams is shown in **Table 6-9** and the table of exchangeable heat loads (TEHL) for indirect process cold streams is shown in **Table 6-10**. Cascade and revised cascade diagrams for the indirect production process can be found in **Fig. 6-10** and **Fig. 6-11**, respectively.

Table 6-9 The table of exchangeable heat loads (TEHL) for indirect process hot streams.

Interval	Load of H1 (kW)	Load of H2 (kW)	Load of H3 (kW)	Load of H4 (kW)	Total Load (kW)
1	-	-	-	-	-
2	-	-	-	-	-
3	-	-	353.23	-	353.23
4	-	-	529.85	-	529.85
5	-	-	5475.1	-	5475.1
6	-	-	883	2018.47	2901.47
7	-	-	8654.2	19781	28435.2
8	-	204.7	883	2018.47	3106.47
9	-	2702	11656.66	26643.84	41002.5
10	-	614	2649.24	6055.42	9318.66
11	-	2190.27	9448.96	21597.66	33236.89
12	-	184.23	794.77	-	979
13	-	20.47	-	-	20.47
14	-	184.23	-	-	184.23
15	-	311.14	-	-	311.14
16	369.5	-	-	-	369.5
17	3835.33	-	-	-	3835.33
18	3768.83	-	-	-	3768.83
19	-	-	-	-	-

Table 6-10. The table of exchangeable heat loads (TEHL) for indirect process cold streams.

Interval	Load of C1 (kW)	Load of C2 (kW)	Load of C3 (kW)	Load of C4 (kW)	Load of C5 (kW)	Load of C6 (kW)	Total Load (kW)
1	-	191580.6	-	-	-	-	191580.6
2	-	3921.24	3193.84	-	-	-	7115
3	-	448.14	365	-	-	-	813.14
4	-	672.22	547.15	-	-	79.5	1298.87
5	-	6946.2	5657.66	-	-	821.6	13425.46
6	-	1120.36	912.53	-	-	132.52	2165.41
7	-	10979.48	8942.75	-	25482.68	1298.7	46703.61
8	-	1120.36	912.53	-	2600.27	132.52	4765.68
9	-	14788.68	12045.34	35873.4	34323.6	1749.15	98780.17
10	-	3361	2737.58	8153	7800.82	-	22052.4
11	-	11987.8	9764	29079.2	-	-	50831
12	-	1008.32	821.275	2445.91	-	-	4275.5
13	-	112	91.25	271.77	-	-	475
14	-	1008.32	821.275	-	-	-	1829.6
15	688.2	-	-	-	-	-	688.2
16	452.77	-	-	-	-	-	452.77
17	5605.26	-	-	-	-	-	5605.26
18	-	-	-	-	-	-	-
19	-	-	-	-	-	-	-

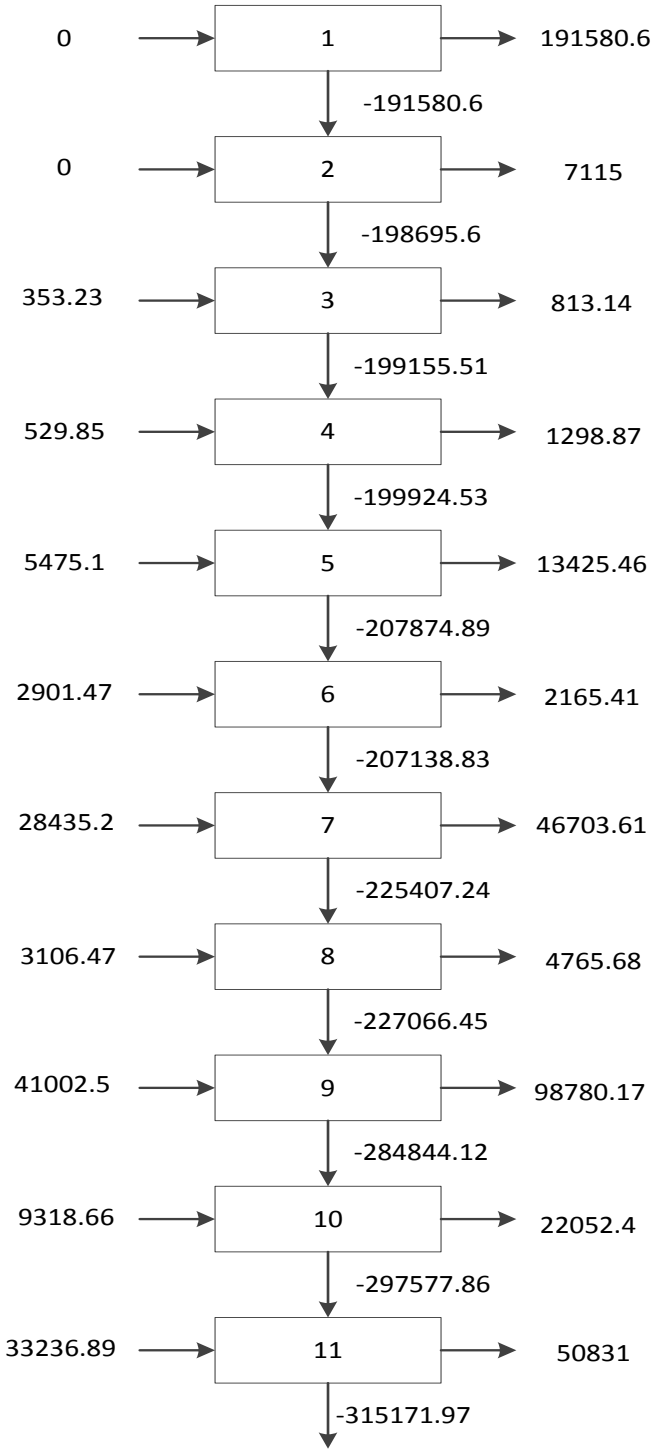

Fig. 6-10 Cascade diagram for the indirect production process.

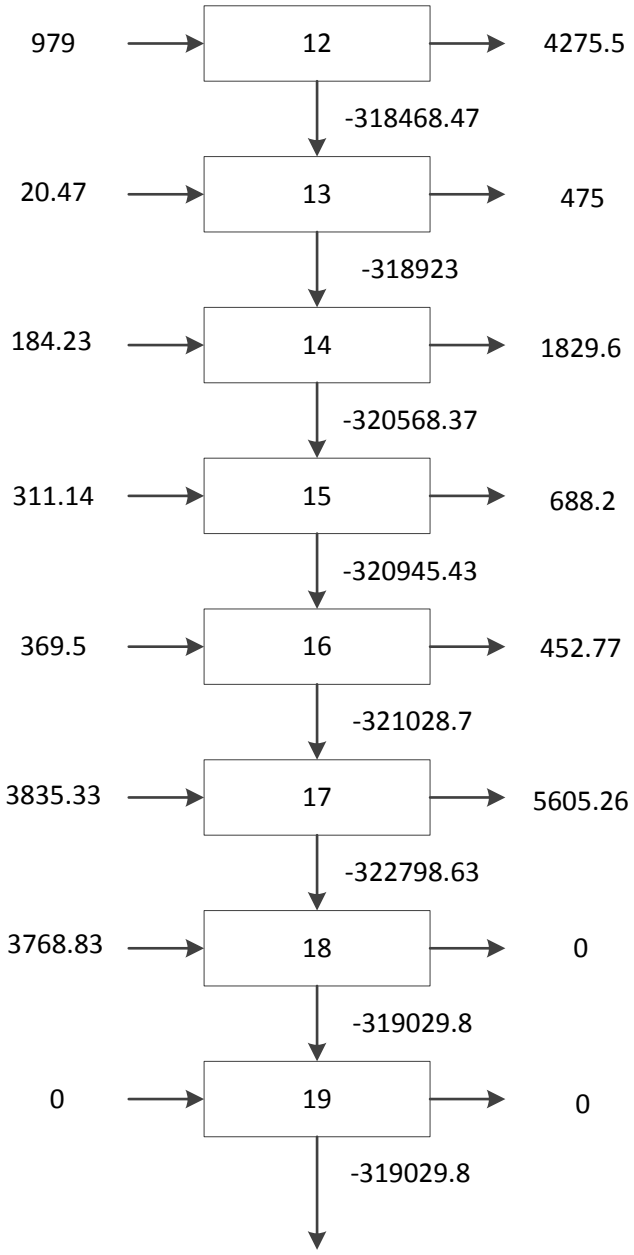

Fig. 6-10. Continued.

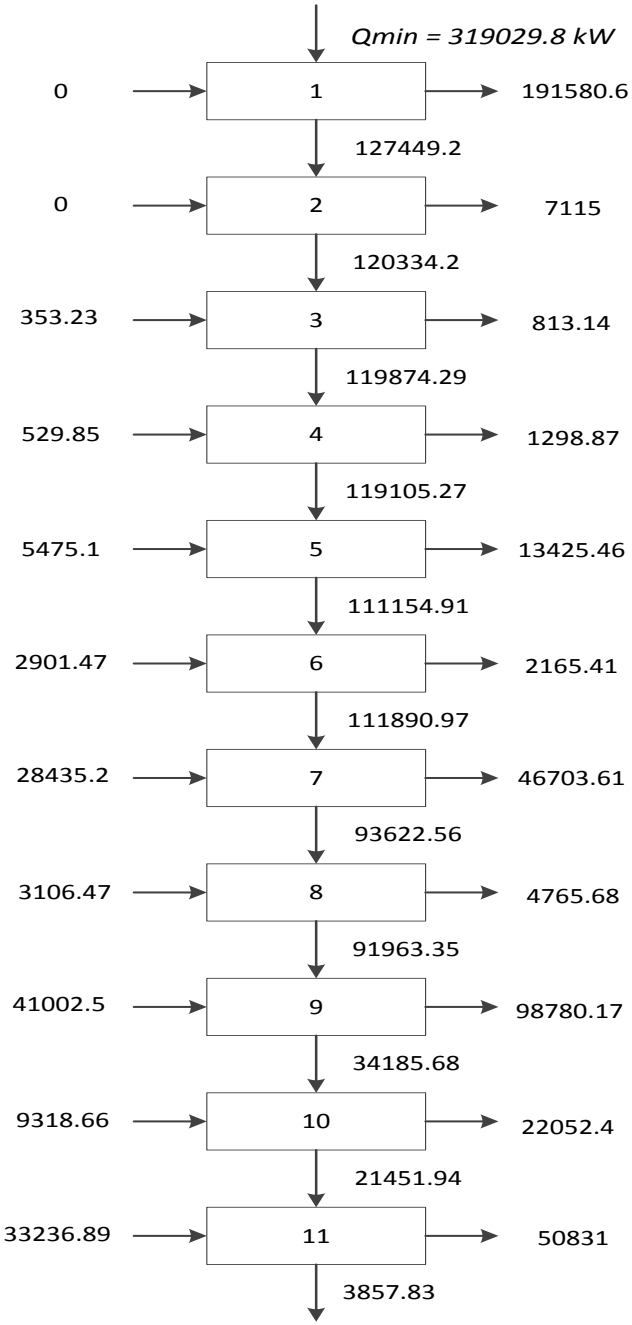

Fig. 6-11 Revised Cascade diagram for the indirect production process.

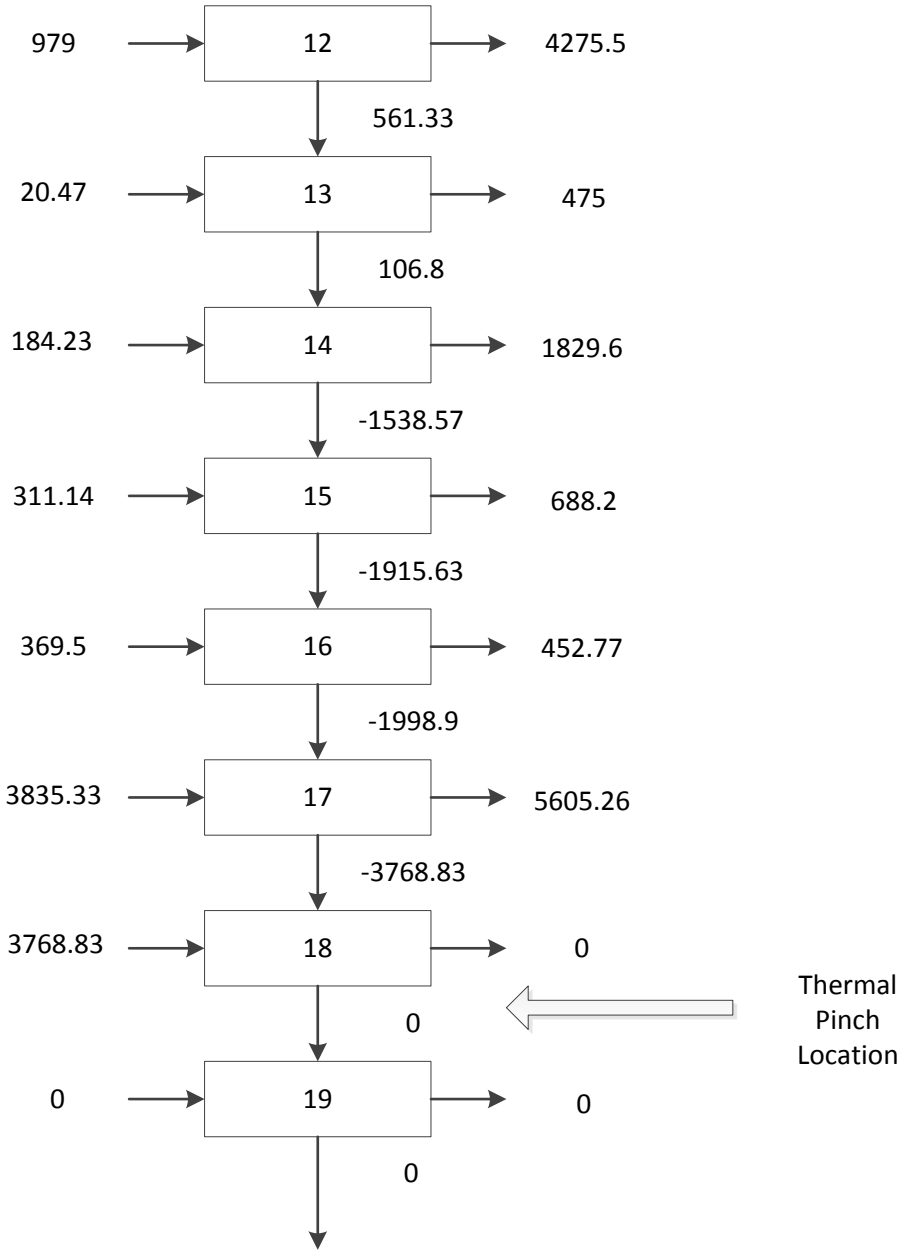

Fig. 6-11. Continued.

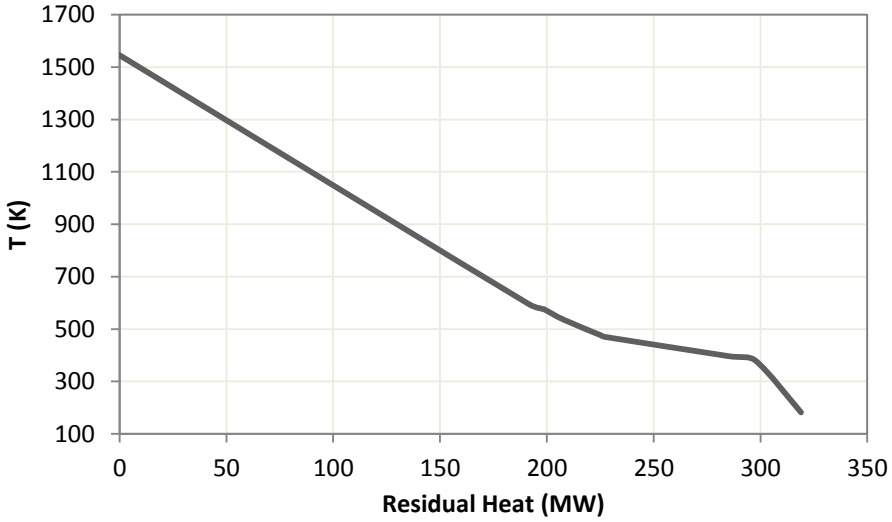

Fig. 6-12 Grand composite curve for heat integration of the indirect process.

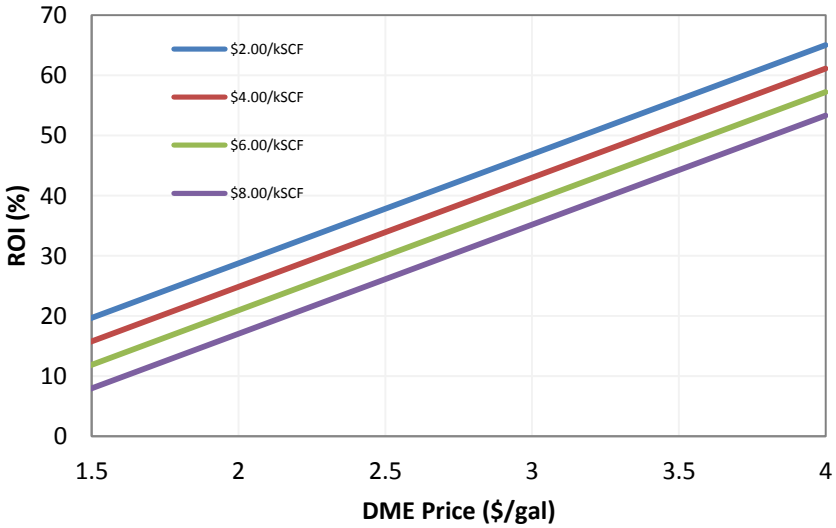

Fig. 6-13 Sensitivity analysis of the indirect process after energy integration.

7 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

This work has addressed process design, simulation and integration of DME production from shale gas by direct and indirect methods. The shale gas feedstock was taken from one of the wells in Barnett shale play. The DME production capacities of the base cases for the direct and indirect processes were set to 3,250 tonnes per day. The direct and indirect process flowsheets were synthesized using five and seven main processing steps, respectively. In the direct method, a combination of partial oxidation and dry reforming was applied in reformer to reach a syngas H_2: CO ratio of 0.7. On the other hand, a combination of partial oxidation and water-gas shift reaction was used in the indirect method to produce syngas that has H_2: CO ratio of 2.0. ASPEN Plus was used to carry out the process simulation studies. Pinch analysis was used to conduct heat integration of the process.

The following are key results obtained from the work:

(1) The capital investment of the direct production method is 25% less than the indirect method. (2) For DME selling price of $2.26/gal and shale gas price of $4.50/kSCF, the ROI of the direct method is 43.24% and for the indirect method is 26%. Consequently, the direct method is more economically attractive than the indirect method. When a sensitivity analysis is considered, the prices of methanol and shale gas are the most important factors impacting the operating cost. (3) The contribution of energy integration on the ROI of the direct method is approximately 2.25%. The ROI of the indirect method is improved by 1.83% after energy integration. (4) Water can show significant importance dependingss on the plant location. Thus, the consumption and

production of water is one of the key criteria to compare these two methods. In contrast to the other criteria, the indirect way has significant advantage over the direct way by producing almost 1760 ton/d water. On the other hand, the direct way produces 35.1 ton/d water. (5) The capture and transformation of CO_2 to other chemicals and chemicals play an important role in environmental impact. The direct method produces less CO_2 emission than the indirect method because it uses dry reforming to convert CO_2 to syngas.

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